Journal of
THE CHEMICAL SOCIETY

Publication Committee

Chairman: C. K. Ingold, D.Sc., F.R.I.C., F.R.S.

C. C. Addison, D.Sc., Ph.D., F.R.I.C.
G. Baddeley, Ph.D., D.Sc., F.R.I.C.
D. H. R. Barton, D.Sc., F.R.I.C., F.R.S.
F. Bergel, D.Phil.Nat., D.Sc., F.R.I.C.
E. Boyland, D.Sc., Ph.D.
J. Chatt, M.A., Sc.D., F.R.I.C.
P. B. D. de la Mare, D.Sc., Ph.D.
H. J. Emeléus, D.Sc., A.R.C.S., F.R.S.
D. H. Everett, M.B.E., M.A., D.Phil., F.R.S.E.
G. Gee, Sc.D., A.R.I.C., F.R.S.
B. A. Hems, D.Sc., F.R.I.C.
E. L. Hirst, M.A., D.Sc., LL.D., F.R.S.
H. R. Ing, M.A., D.Phil., F.R.S.
H. M. N. H. Irving, M.A., D.Phil., F.R.I.C.
D. J. G. Ives, D.Sc., A.R.C.S., F.R.I.C.
E. R. H. Jones, D.Sc., F.R.I.C., F.R.S.
G. W. Kenner, M.Sc., Ph.D.
H. C. Longuet-Higgins, M.A., D.Phil.
B. Lythgoe, M.A., Ph.D., F.R.I.C.
R. A. Morton, D.Sc., Ph.D., F.R.S.
A. Neuberger, Ph.D., M.D., F.R.S.
R. G. W. Norrish, Sc.D., F.R.I.C., F.R.S.
M. W. Perrin, C.B.E., M.A., F.R.I.C.
V. Petrow, Ph.D., D.Sc., F.R.I.C.
H. M. Powell, M.A., B.Sc., F.R.S.
P. L. Robinson, D.Sc., F.R.I.C.
K. Schofield, Ph.D., D.Sc., F.R.I.C.
N. Sheppard, M.A., Ph.D.
M. Stacey, Ph.D., D.Sc., F.R.S.
L. E. Sutton, M.A., D.Phil., F.R.S.
H. W. Thompson, M.A., D.Sc., F.R.S.
E. E. Turner, M.A., D.Sc., F.R.S.
A. R. J. P. Ubbelohde, M.A., D.Sc., F.R.S.

Editor

R. S. Cahn, M.A., D.Phil.Nat., F.R.I.C.

Assistant Editors

A. D. Mitchell, D.Sc., F.R.I.C.
L. C. Cross, Ph.D., A.R.C.S., F.R.I.C.
A. E. Somerfield, Ph.D.

DECEMBER, 1956

Subscription rate to non-Fellows £10 0*s.* 0*d.* per annum post free.

LONDON: THE CHEMICAL SOCIETY, BURLINGTON HOUSE, W.1

THE CHEMICAL SOCIETY

PATRON
HER MAJESTY THE QUEEN

President
E. L. Hirst, M.A., D.Sc., LL.D., F.R.S.

Vice-Presidents
who have filled the office of President

Sir Ian Heilbron, D.S.O., D.Sc., LL.D., F.R.S.
Sir Cyril Hinshelwood, M.A., Sc.D., F.R.S.
C. K. Ingold, D.Sc., F.R.I.C., F.R.S.
W. H. Mills, M.A., Sc.D., F.R.S.
Sir Eric Rideal, M.B.E., M.A., D.Sc., F.R.S.
W. Wardlaw, C.B.E., D.Sc., F.R.I.C.

Vice-Presidents

E. D. Hughes, D.Sc., F.R.I.C., F.R.S.
E. R. H. Jones, D.Sc., F.R.I.C., F.R.S.
R. P. Linstead, C.B.E., M.A., D.Sc., F.R.S.
H. W. Melville, D.Sc., F.R.I.C., F.R.S.
M. Stacey, Ph.D., D.Sc., F.R.S.
Sir Alexander Todd, M.A., D.Sc., F.R.S.

Honorary Treasurer
M. W. Perrin, C.B.E., M.A., F.R.I.C.

Honorary Secretaries

L. E. Sutton, M.A., D.Phil., F.R.S.
F. Bergel, D.Phil.Nat., D.Sc., F.R.I.C.
J. Chatt, M.A., Sc.D., F.R.I.C.

Ordinary Members of Council

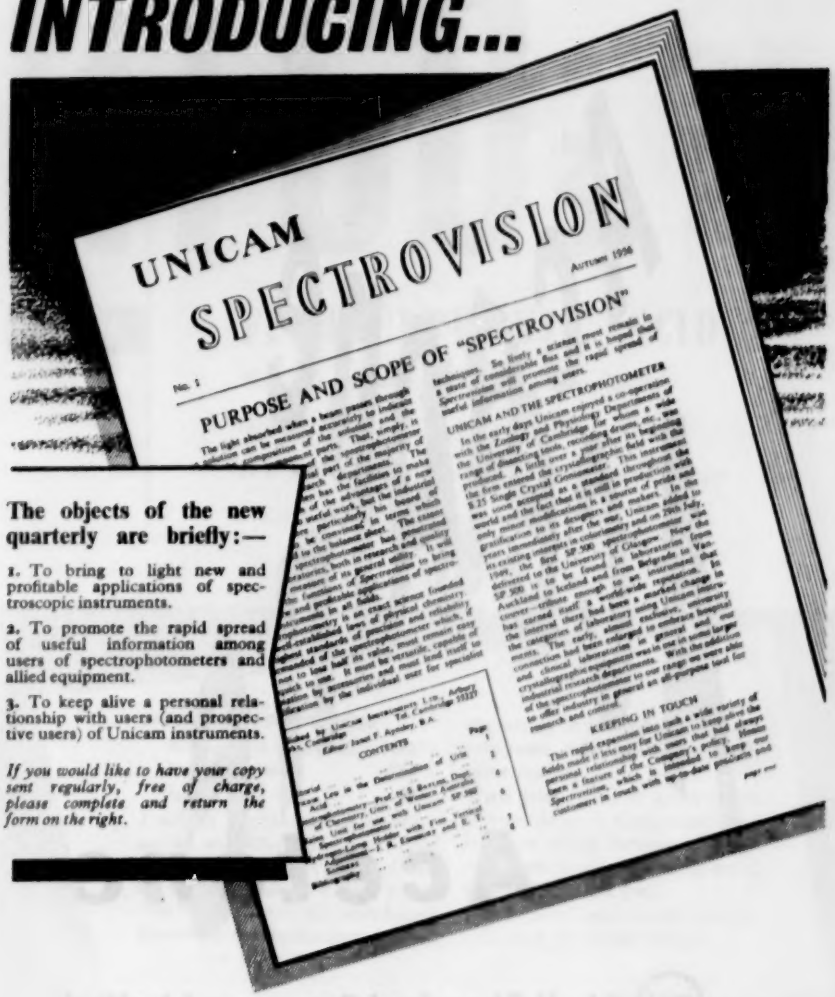
D. W. Adamson, M.Sc., D.Phil., A.R.I.C.
C. C. Addison, D.Sc., Ph.D., F.R.I.C.
G. R. Barker, B.Sc., Ph.D.
R. M. Barrer, D.Sc., Sc.D., F.R.S.
V. C. Barry, D.Sc., M.R.I.A., F.I.C.I., F.R.I.C.
F. Bell, D.Sc., F.R.I.C., F.R.S.E.
A. G. Evans, Ph.D., D.Sc., F.R.I.C.
W. Gerrard, D.Sc., Ph.D., F.R.I.C.
A. Hickling, D.Sc., Ph.D., F.R.I.C.
L. Hunter, Ph.D., D.Sc., F.R.I.C.
H. M. N. H. Irving, M.A., D.Phil., F.R.I.C.
G. W. Kenner, M.Sc., Ph.D.
B. Lythgoe, M.A., Ph.D., F.R.I.C.
A. Maccoll, M.Sc., Ph.D.
F. H. Pollard, B.Sc., Ph.D.
J. M. Robertson, M.A., D.Sc., F.R.S.
H. N. Rydon, D.Sc., D.Phil., F.R.I.C.
H. D. Springall, M.A., D.Phil., F.R.I.C.
L. A. K. Staveley, M.A.
W. Wild, B.Sc., Ph.D., A.R.I.C.
G. T. Young, Ph.D., M.A., A.R.I.C.

General Secretary
J. R. Ruck Keene, M.B.E., T.D., M.A.

Librarian
R. G. Griffin, F.L.A.

Deputy Librarian
J. Bird

INTRODUCING...



The objects of the new quarterly are briefly:—

1. To bring to light new and profitable applications of spectroscopic instruments.

2. To promote the rapid spread of useful information among users of spectrophotometers and allied equipment.

3. To keep alive a personal relationship with users (and prospective users) of Unicam instruments.

If you would like to have your copy sent regularly, free of charge, please complete and return the form on the right.

UNICAM
SPECTROPHOTOMETERS

I wish my name to be included in the mailing list for Spectrovision.

SIGNED _____

NAME _____

TITLE _____

ADDRESS _____

_____

J.C.

UNICAM INSTRUMENTS LIMITED ARBURY WORKS CAMBRIDGE

Shell Chemical Company Limited

Norman House, 105-109 Strand, London, W.C.2. Telephone: Temple Bar 4455

Sales Offices:
LONDON: Walter House, Bedford Street, W.C.2. *Tel: Temple Bar 4455.*
MANCHESTER: 144-146 Deansgate. *Tel: Deansgate 6451.*
BIRMINGHAM: 14-20 Corporation St., 2. *Tel: Midland 6954-8.*
GLASGOW: 124 St. Vincent Street, C.2. *Tel: Glasgow Central 9561.*
BELFAST: 35-37 Boyne Square. *Tel: Belfast 20081.*
DUBLIN: 53 Middle Abbey Street. *Tel: Dublin 45775.*

$HFSO_3$

FLUOSULPHONIC ACID

This is a colourless or pale straw-coloured, mobile, liquid which fumes in moist air.

It is a remarkably stable compound and can be redistilled in glass apparatus.

PHYSICAL PROPERTIES

Boiling point at 760mm.	163°C.
Freezing point	−87.3°C.
Sp. Gr. at 15.6°C.	1.743

Used as a catalyst in condensation and alkylation reactions; for the preparation of alkyl and aryl fluosulphonates, acyl fluorides and aromatic sulphonyl fluorides. As a tool in preparative chemistry, it is similar to chlorosulphonic acid but is generally more stable.

With boric acid it gives boron trifluoride in an easily controlled reaction which forms a convenient method of generating small amounts of that gas.

It has been used in the electropolishing of certain metals.

Advice on materials of construction and on handling, may be obtained from

IMPERIAL SMELTING

U.K. MEMBER OF THE CONSOLIDATED ZINC CORPORATION LIMITED

IMPERIAL SMELTING CORPORATION (SALES) LTD., 37 DOVER ST., LONDON, W.1

PIONEERS IN FLUORINE DEVELOPMENT

THE WORLD'S GREATEST BOOKSHOP

FOYLES
• FOR BOOKS •

ALL YOUR CHRISTMAS
Gift Books

FAMED CENTRE FOR
Technical Books
★

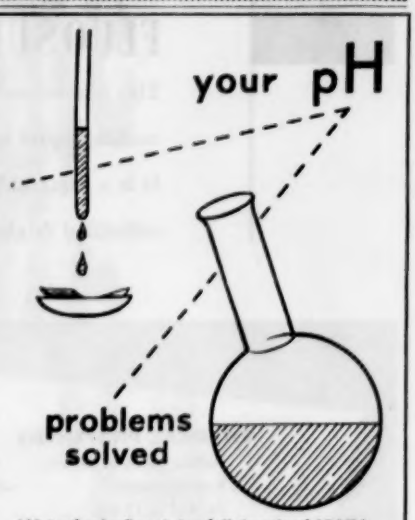
119-125 CHARING CROSS ROAD, LONDON, W.C.2
GERrard 5660 (20 lines) ★ Open 9-6 (inc. Sat.)
Two minutes from Tottenham Court Rd. Station

We are makers of:

TRICHLOROACETIC ACID B.P.

Samples and quotations from:

KAYLENE (CHEMICALS) LTD.
WATERLOO ROAD, LONDON, N.W.2
TEL: GLADSTONE 1071/2/3



Write for leaflet giving full details of JOHNSON UNIVERSAL AND COMPARATOR TEST PAPERS for quick and accurate determination of pH values from 3·6 to 10 pH.

JOHNSONS OF HENDON LTD
LONDON, N.W.4

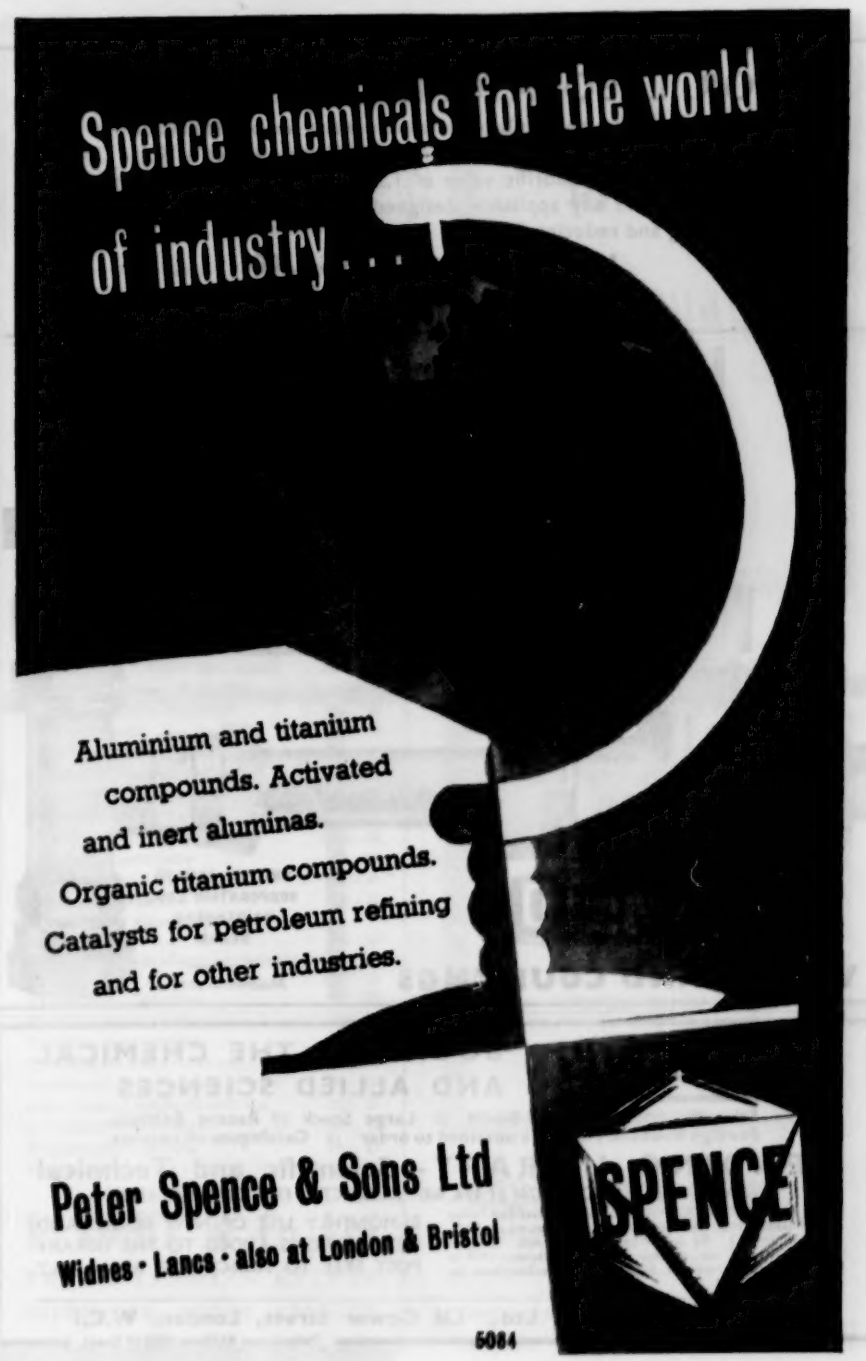
QUARTERLY REVIEWS

Back Numbers

Vol. I (1947)–Vol. X (1956)

Price £1 10s. per volume may be obtained from:

THE CHEMICAL SOCIETY Burlington House · London, W.1


Spence chemicals for the world of industry...
Aluminium and titanium compounds. Activated and inert aluminas.
Organic titanium compounds.
Catalysts for petroleum refining and for other industries.
Peter Spence & Sons Ltd
Widnes • Lancs • also at London & Bristol
SPENCE
5084

MANSFIELD OIL-GAS PLANT
FOR LABORATORIES' GAS SUPPLY

Laboratories without a supply of gas should write for particulars of this Plant which produces gas in a simple manner from any cheap oil such as Solar Oil. . . . The gas produced has a calorific value of 1,350 B.T.U.'s per cubic foot, and is suitable for use with any appliance designed for use with coal gas and gives perfect oxidising and reducing flames.

MANSFIELD & SONS LTD
62 HAMILTON SQUARE, BIRKENHEAD

TODAY, MORE THAN EVER,
INDUSTRY LOOKS TO ERMETO

for efficiency in pipe line systems

Whatever the field of application, whether it involves high pressures or very low pressure vacuum lines, ERMETO fittings are successfully withstanding the increased stresses imposed by higher industrial efficiency.

We shall be glad to send technical details on request.

ERMETO

VALVES AND COUPLINGS

BRITISH ERMETO CORPORATION LTD., MAIDENHEAD, BERKS.
Telephone: Maidenhead 2271–4

H. K. LEWIS
BOOKS ON THE CHEMICAL AND ALLIED SCIENCES

Scientific and Technical Books :: Large Stock of Recent Editions.
Foreign Books not in Stock obtained to order :: Catalogues on request.

LENDING LIBRARY—Scientific and Technical

ANNUAL SUBSCRIPTION FROM £1 17s. 6d. PROSPECTUS FREE ON APPLICATION

THE LIBRARY CATALOGUE containing classified Index of Authors and Subjects revised to December 1949. Pp. xii + 1152. To subscribers 17s. 6d. net. To non-subscribers 35s. net., postage 1s. 8d. Supplement 1950 to 1952. To subscribers 1s. 6d. net; to non-subscribers 3s. net; postage 9d.

BI-MONTHLY LIST OF NEW BOOKS AND NEW EDITIONS ADDED TO THE LIBRARY POST FREE TO SUBSCRIBERS REGULARLY

H. K. LEWIS & Co. Ltd., 136 Gower Street, London, W.C.1
Telephone: EUSton 4282 (7 lines)

Latest additions to 1956 Catalogue

Acetovanillone	**12/- H**
5-Amino *iso*phthalic acid	**75/- H**
DL-Benzoyl-α-alanine	**42/- H**
DL-ε-Benzoyllysine	**50/- H**
DL-Benzoyl phenylalanine	**37/- D**
DL-Benzoylvaline	**90 - H**
Bromoacetal (bromoacetaldehyde diethyl acetal)	**44/- H**
1-Bromo-2-naphthol	**21/- D**
2-Chlorocyclohexanone	**60/- H**
6-Chloropurine	**43/- d**
Convallamarin	**8/- G**
L-Cysteine hydantoin	**63/- D**
L-Cystine hydantoin	**52/- D**
4 : 5-Diamino-pyrimidine	**50/- d**
L-Dibenzoylcystine	**84/- D**
2 : 5-Dibromothiophene	**48/- H**
α : β-Dichloro-propionic acid	**82/- H**
Dicyclopropyl ketone	**109/- H**
L-Diformylcystine	**91/- D**
2 : 4-Dimethoxy-benzaldehyde	**120/- H**
2 : 4-Dimethyl thiazole	**35/- D**
L-Diphenacetylcystine	**59/- D**
Diphenyl phosphoryl chloride	**42/- H**
Ethyl *iso*butyl ketone	**170/- H**
2-Ethyl hexoic acid	**32/- K**
Flavin adenine dinucleotide (FAD)(85% ± 5%)(25 mgm. amps.)	**138/- A**
Hexamethylene dibromide	**40/- H**
Hexamethylene dinitrile	**93/- H**
Hydrobenzoin	**35/- D**
***p*-Hydroxy-phenylacetic acid**	**39/- D**
L-Leucine (free from methionine)	**62/- H**
Methyl formanilide	**150/- K**
***O*-Methyl-DL-serine**	**6/- G**
***N*-Morpholylacetal**	**155/- H**
***m*-Nitrobenzonitrile**	**36/- D**
4-Nitropyridine-*N*-oxide	**19/- D**
5-Nitro-quinoline	**38/- D**
Potassium phenolphthalein disulphate	**50/- D**
Pyridine-2-aldoxime methiodide (2-PAM)	**197/- G**
Pyridine-2-aldoxime	**65/- H**
Pyridine-3-aldoxime	**80/- H**
Pyridine-4-aldoxime	**75/- H**
Pyridine-2 : 6-dialdoxime	**110/- H**
Pyridoxal-5′-phosphate (cryst.)	**96/- G**
Quinoline-*N*-oxide dihydrate	**28/- D**
***m*-Sulphobenzoic acid**	**20/- D**
Triphenylphosphine	**44/- D**
Vitamin A alcohol (synthetic, cryst.)	**33/- G**

L. LIGHT & Co Ltd

POYLE TRADING ESTATE

COLNBROOK BUCKS ENGLAND

Lithium Carbonate 98/99%

BRITISH MANUFACTURE

COMPETITIVE PRICES

BULK PRODUCTION

PROMPT DELIVERIES

FROM STOCK

ASSOCIATED LEAD

MANUFACTURERS LIMITED

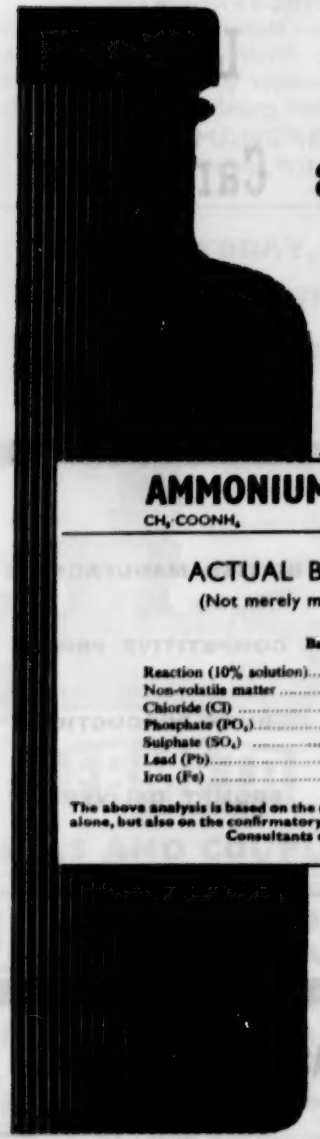
SPECIAL CHEMICALS DIVISION

CRESCENT HOUSE, NEWCASTLE UPON TYNE, 1

the outstanding purities of

Judactan

analytical reagents



We invite you to compare the actual batch analysis shown here, with the purities guaranteed by the specifications to which you normally work — we are sure the comparison will be helpful to you.

AMMONIUM ACETATE A.R.

CH_3COONH_4 Mol. Wt. 77·08

ACTUAL BATCH ANALYSIS

(Not merely maximum impurity values)

Batch No. 10531

Reaction (10% solution)	pH6·7
Non-volatile matter	0·0025%
Chloride (Cl)	0·0003%
Phosphate (PO_4)	0·0002%
Sulphate (SO_4)	0·0015%
Lead (Pb)	0·00006%
Iron (Fe)	0·00005%

The above analysis is based on the results, not of our own Control Laboratories alone, but also on the confirmatory Analytical Certificate issued by independent Consultants of international repute

This is the analysis of a Judactan reagent. And, as with every other reagent in the series it is the *actual batch analysis* — it is one of several of which we are especially proud.

The General Chemical & Pharmaceutical Co. Ltd., Chemical Manufacturers, Judex Works, Sudbury, Middlesex.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

General, Physical, and Inorganic.

PAGE

918. Co-ordination Compounds between Ethylenediaminetetra-acetic Acid and Gallium, Indium, and Thallium.
By KAZUO SAITO and (the late) HENRY TERREY 4701

919. Observations on Ammonium Ferric Disulphate Dodecahydrate (Ammonium Ferric Alum) and Some of its Derivatives.
By HENRY BASSETT 4705

921. Structure and Reactivity of the Oxyanions of Transition Metals. Part II. Investigations by Electron-spin Resonance.
By A. CARRINGTON, D. J. E. INGRAM, D. SCHONLAND, and M. C. R. SYMONS . . 4710

925. Kinetics of the Decarboxylation of Oxaloacetic Acid.
By E. GELLES 4736

944. Adsorption from Binary Liquid Mixtures on Activated Alumina.
By J. J. KIPLING and D. B. PEAKALL 4828

945. Crystal Symmetry, and the Adsorption of Dyes by Growing Crystals. Part I. Ammonium Nitrate IV.
By JOHN WHETSTONE 4841

946. A Polarographic Study of Copper Malonate Complexes.
By E. GELLES and G. H. NANCOLLAS 4847

952. Nucleotides. Part XXXIX. 5′-Deoxy-5′-iodo-O^2 : 2′-*cyclo*uridine : an *X*-Ray Crystallographic Study.
By D. M. BROWN, W. COCHRAN, E. H. MEDLIN, and S. VARADARAJAN . . . 4873

954. The Crystal and Molecular Structure of Thianthren.
By H. LYNTON and (in part) E. G. COX 4886

955. *d*-Orbital Contraction in Chemical Bonding.
By D. P. CRAIG and E. A. MAGNUSSON 4895

957. Germanium Esters. Part I. Parachors and Molecular Structure.
By D. C. BRADLEY, L. J. KAY, and W. WARDLAW 4916

961. Water-soluble Complexes of Niobium (Columbium) and Tantalum. Part I. Complexes with α-Hydroxy-acids and (2-Hydroxyethyl)amines.
By FRED FAIRBROTHER and JOHN B. TAYLOR 4946

NOTE:

968. Spectra of Transition-metal Complexes of the Type $[Co(NH_3)_5X]^{2+}$.
By J. S. GRIFFITH and L. E. ORGEL 4981

Physical Organic.

931. The Polycondensation of Benzyl Chloride catalysed by Stannic Chloride.
By L. VALENTINE and R. W. WINTER 4768

932. The Polarography of Some Simple Pyrazine Derivatves.
By L. F. WIGGINS and W. S. WISE 4780

939. The Infrared Absorption Spectra of the Carbonyl Group in Methoxyanthraquinones, and in the Hydrochlorides of 1-Methoxyanthraquinones.
By L. A. WILES and L. C. THOMAS. 4811

948. The Structure of Molecular Compounds. Part XI. Crystal Structure of the Addition Complex of Quinol and Methyl Cyanide.
By S. C. WALLWORK and H. M. POWELL 4855

949. Aromatic Reactivity. Part I. Effects of Substituents on the Acid Cleavage of Phenyltrimethylsilanes.
By C. EABORN 4858

950. Phosphorescence and Fluorescence of Some Aromatic Nitro-amines.
By R. FOSTER, D. LL. HAMMICK, G. M. HOOD, and A. C. E. SANDERS 4865

PAGE

951. Infrared Spectra of Natural Products. Part VI. The Characterization of Equatorial and Axial 3-Hydroxyl Groups in Triterpenoids.
By (Miss) I. L. Allsop, A. R. H. Cole, D. E. White, and R. L. S. Willix . . 4868

953. The Equilibrium in the System : Water–6-Hexanolactam (ε-Caprolactam) .
By A. B. Meggy 4876

958. Radical-capture Agents in Tetralin. Measurement of Relative Efficiencies and Correlation with Structure.
By D. S. Davies, H. L. Goldsmith, A. K. Gupta, and G. R. Lester . . . 4926

959. Kinetics and Mechanism of Bromination of Phenol with Bromine and Iodine Bromide in Glacial Acetic Acid and Carbon Tetrachloride.
By Lourdu M. Yeddanapalli and N. S. Gnanapragasam 4934

962. Search for Spectral Evidence of Expansion of the Valency Shell of Sulphur in Aromatic Sulphides.
By A. Mangini and R. Passerini 4954

963. Energy Levels and Absorption of Some Monosubstituted Benzene Derivatives.
By A. Mangini and C. Zauli 4960

Organic.

920. A New Synthesis of 2 : 3 : 5 : 6-Substituted 4-Pyrimidones.
By Benjamin Staskun and Henry Stephen 4708

922. Picrotoxin and Tutin. Part VIII.
By R. B. Johns, S. N. Slater, and R. J. Woods (with, in part, D. Brasch and Roy Gee) 4715

923. Two Hypothetical Metabolites of Proguanil (" Paludrine ").
By R. M. Acheson and N. F. Taylor 4727

924. Several Quinoxalines of Biological Interest.
By R. M. Acheson. 4731

926. By-ways of Synthesis of Cortisone from Hecogenin. Part I. 9 : 11-Dehydrohecogenin as Intermediate in Preparation of 11-Oxygenated Compounds (11-Oxotigogenin and 3β-Acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione).
By R. K. Callow and V. H. T. James 4739

927. By-ways of Synthesis of Cortisone from Hecogenin. Part II. A Route to 11-Oxygenated Compounds through 3β : 20β-Diacetoxy-11-bromo*allo*pregnan-12-one.
By R. K. Callow and V. H. T. James 4744

928. The Structure and Stereochemistry of Tazettine.
By T. Ikeda, W. I. Taylor, Y. Tsuda, S. Uyeo, and H. Yajima. 4749

929. Researches on Acetylenic Compounds. Part LIII. The Relative Strengths of Some Unsaturated Carboxylic Acids.
By G. H. Mansfield and M. C. Whiting 4761

930. Researches on Acetylenic Compounds. Part LIV. The Preparation and Synthetical Applications of Ethynylmagnesium Bromide.
By E. R. H. Jones, L. Skatteböl, and M. C. Whiting 4765

933. Experiments on the Preparation of Indolocarbazoles. Part IX. The Preparation of 9-Methylindolo(2′ : 3′-1 : 2)carbazole.
By R. J. Brunton, F. K. Drayson, (the late) S. G. P. Plant, and Muriel L. Tomlinson 4783

934. Reactions of Organic Peroxides. Part VIII. 1 : 3 : 3-Trimethylindan-1-yl Hydroperoxide and its Conversion into 2 : 4 : 4-Trimethylchroman Derivatives.
By William Webster and Donald P. Young. 4785

935. Derivatives of Thionaphthen. Part II. Thionaphthen Derivatives formed by Cyclisation of Acetonyl Aryl Sulphides and Aryl Phenacyl Sulphides.
By J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton . . 4791

936. Quantitative Microestimation of Formaldehyde in the Presence of Periodate and its Application to the Structural Examination of Carbohydrate Phenylosazones.
By L. Hough, D. B. Powell, and B. M. Woods 4799

937. Aryldihydroresorcinols. Part II. The Influence of the Nitro-group in Dihydro-5-*o*-nitrostyrylresorcinol.
By E. E. Ayling and D. A. Davies. 4803

938. The Degradation of Xylobiose and Xylotriose by Alkali.
By G. O. Aspinall, (Miss) Mary E. Carter, and (in part) M. Los . . . 4807

PAGE

940. The Formation of Osazones during Attempted Fischer Indole Syntheses.
By D. A. Kinsley and (the late) S. G. P. Plant 4814

941. Steroids and Walden Inversion. Part XXXIV. Solvolysis of Chloesteryl Toluene-*p*-sulphonate with Thiophenoxide Ions.
By C. W. Shoppee, H. C. Richards, and G. H. R. Summers 4817

942. Steroids and Walden Inversion. Part XXXV. *NN*-Dimethylcholest-7-en-3α- and -3β-ylamine.
By D. E. Evans and G. H. R. Summers 4821

943. Urinary Steroids and Related Compounds. Part I. 11-Substituted Derivatives of Androsterone.
By W. Klyne and Sheila Ridley 4825

947. Quassin and *neo*Quassin. Part V.
By R. J. S. Beer, B. G. Dutton, D. B. Jaquiss, Alexander Robertson, and W. E. Savige 4850

956. Hydroaromatic Steroid Hormones. Part V. Some D-Homo-18 : 19-bisnorsteroids.
By A. J. Birch and Herchel Smith 4909

960. The Interaction of Alkylbenzenes with Excess of Friedel–Crafts Acetylating Agent.
By G. Baddeley and E. Wrench 4943

964. Coenzyme A. Part X. Model Experiments on the Synthesis of Pyrophosphates of *N*-Pantoylamines. New Methods for the Debenzylation of Esters of Pyrophosphoric Acid.
By J. Arris, J. Baddiley, J. G. Buchanan, and E. M. Thain 4968

965. A Molecular Rearrangement during the Reduction of Thionaphthenopyrazole Dioxides.
By W. J. Barry, I. L. Finar, and Alma B. Simmonds 4974

Notes:

966. Synthesis of a Dihydrosantonin Isomer.
By J. K. Chakrabarti, P. Dutt, and P. C. Dutta 4978

967. Lactones. Part IV. A New Preparation of 7-Ethoxy-6-methoxyphthalide.
By W. R. Logan and G. T. Newbold 4980

969. 2-Acyl Derivatives of Cyclic 1 : 3-Diones. Part IV. The Structure of Dehydroleptospermone.
By W. R. Chan and C. H. Hassall 4983

970. 3-Hydroxythiophen.
By M. C. Ford and Donald Mackay 4985

971. The Fission of Alkyl Allyl Ethers by Boron Trichloride.
By W. Gerrard, M. F. Lappert, and H. B. Silver 4987

INDEX OF AUTHORS' NAMES.

Acheson, R. M., 4731.
Acheson, R. M., and Taylor, N. F., 4727.
Allsop, I. L., Cole, A. R. H., White, D. E., and Willix, R. L. S., 4868.
Arris, J., Baddiley, J., Buchanan, J. G., and Thain, E. M., 4968.
Aspinall, G. O., Carter, M. E., and Los, M., 4807.
Ayling, E. E., and Davies, D. A., 4803.
Baddeley, G., and Wrench, E., 4943.
Baddiley, J. See Arris, J., 4968.
Banfield, J. E., Davies, W., Gamble, N. W., and Middleton, S. 4791.
Barry, W. J., Finar, I. L., and Simmonds, A. B., 4974.
Bassett, H., 4705.
Beer, R. J. S., Dutton, B. G., Jaquiss, D. B., Robertson, A., and Savige, W. E., 4850.
Birch, A. J., and Smith, H., 4909.
Bradley, D. C., Kay, I. J., and Wardlaw, W., 4916.
Brash, D. See Johns, R. B., 4715.
Brown, D. M., Cochran, W., Medlin, E. H., and Varadarajan, S., 4873.
Brunton, R. J., Drayson, F. K., Plant, S. G. P., and Tomlinson, M. L., 4783.
Buchanan, J. G. See Arris, J., 4968.
Callow, R. K., and James, V. H. T., 4739, 4744.
Carrington, A., Ingram, D. J. E., Schonland, D., and Symons, M. C. R., 4710.
Carter, M. E. See Aspinall, G. O., 4807.
Chakrabarti, J. K., Dutt, P., and Dutta, P. C., 4978.
Chan, W. R., and Hassall, C. H., 4983.
Cochran, W. See Brown, D. M., 4873.
Cole, A. R. H. See Allsop, I. L., 4868.
Cox, E. G. See Lynton, H., 4886.
Craig, D. P., and Magnusson, E. A., 4895.
Davies, D. A. See Ayling, E. E., 4803.
Davies, D. S., Goldsmith, H. L., Gupta, A. K., and Lester, G. R., 4926.

Davies, W. See Banfield, J. E., 4791.
Drayson, F. K. See Brunton, R. J., 4783.
Dutt, P. See Chakrabarti, J. K., 4978.
Dutta, P. C. See Chakrabarti, J. K., 4978.
Dutton, B. G. See Beer, R. J. S., 4850.
Eaborn, C., 4858.
Evans, D. E., and Summers, G. H. R., 4821.
Fairbrother, F., and Taylor, J. B., 4946.
Finar, I. L. See Barry, W. J., 4974.
Ford, M. C., and Mackay, D., 4985.
Foster, R., Hammick, D. Ll., Hood, G. M., and Sanders, A. C. E., 4865.
Gamble, N. W. See Banfield, J. E., 4791.
Gee, R. See Johns, R. B., 4715.
Gelles, E., 4736.
Gelles, E., and Nancollas, G. H., 4847.
Gerrard, W., Lappert, M. F., and Silver, H. B., 4987.
Gnanapragasam, N. S. See Yeddanapalli, L. M., 4934.
Goldsmith, H. L. See Davies, D. S., 4926.
Griffith, J. S., and Orgel, L. E., 4981.
Gupta, A. K. See Davies, D. S., 4926.
Hammick, D. Ll. See Foster, R., 4865.
Hassall, C. H. See Chan, W. R., 4983.
Hood, G. M. See Foster, R., 4865.
Hough, L., Powell, D. B., and Woods, B. M., 4799.
Ikeda, T., Taylor, W. I., Tsuda, Y., Uyeo, S., and Yajima, H., 4749.
Ingram, D. J. E. See Carrington, A., 4710.
James, V. H. T. See Callow, R. K., 4739, 4744.
Jaquiss, D. B. See Beer, R. J. S., 4850.
Johns, R. B., Slater, S. N. Woods, R. J., Brash, D., and Gee, R., 4715.
Jones, E. R. H., Skattebøl, L., and Whiting, M. C., 4765.
Kay, L. J. See Bradley, D. C., 4916.
Kinsley, D. A., and Plant, S. G. P., 4814.
Kipling, J. J., and Peakall, D. B., 4828.
Klyne, W., and Ridley, S., 4825.
Lappert, M. F. See Gerrard, W., 4987.
Lester, G. R. See Davies, D. S., 4926.
Logan, W. R., and Newbold, G. T., 4980.
Los, M. See Aspinall, G. O., 4807.
Lynton, H., and Cox, E. G., 4886.
Mackay, D. See Ford, M. C., 4985.
Magnusson, E. A. See Craig, D. P., 4895.
Mangini, A., and Passerini, R., 4954.
Mangini, A., and Zauli, C., 4960.
Mansfield, G. H., and Whiting, M. C., 4761.
Medlin, E. H. See Brown, D. M., 4873.
Meggy, A. B., 4876.
Middleton, S. See Banfield, J. E., 4791.
Nancollas, G. H. See Gelles, E., 4847.
Newbold, G. T. See Logan, W. R., 4980.
Orgel, L. E. See Griffith, J. S., 4981.
Passerini, R. See Mangini, A., 4954.
Peakall, D. B. See Kipling, J. J., 4828.
Plant, S. G. P. See Brunton, R. J., 4783, and Kinsley, D. A., 4814.
Powell, D. B. See Hough, L., 4799.
Powell, H. M. See Wallwork, S. C., 4855.
Richards, H. C. See Shoppee, C. W., 4817.
Ridley, S. See Klyne, W., 4825.
Robertson, A. See Beer, R. J. S., 4850.
Saito, K., and Terrey, H., 4701.
Sanders, A. C. E. See Foster, R., 4865.
Savige, W. E. See Beer, R. J. S., 4850.
Schonland, D. See Carrington, A., 4710.
Shoppee, C. W., Richards, H. C., and Summers, G. H. R., 4817.
Silver, H. B. See Gerrard, W., 4987.
Simmonds, A. B. See Barry, W. J., 4974.
Skattebøl, L. See Jones, E. R. H., 4765.
Slater, S. N. See Johns, R. B., 4715.
Smith, H. See Birch, A. J., 4909.
Staskun, B., and Stephen, H., 4708.
Stephen, H. See Staskun, B., 4708.
Summers, G. H. R. See Evans, D. E., 4821, and Shoppee, C. W., 4817.
Symons, M. C. R. See Carrington, A., 4710.
Taylor, J. B. See Fairbrother, F., 4946.
Taylor, N. F. See Acheson, R. M., 4727.
Taylor, W. I. See Ikeda, T., 4749.
Terrey, H. See Saito, K., 4701.
Thain, E. M. See Arris, J., 4968.
Thomas, L. C. See Wiles, L. A., 4811.
Tomlinson, M. L. See Brunton, R. J., 4783.
Tsuda, Y. See Ikeda, T., 4749.
Uyeo, S. See Ikeda, T., 4749.
Valentine, L., and Winter, R. W., 4768.
Varadarajan, S. See Brown, D. M., 4873.
Wallwork, S. C., and Powell, H. M., 4855.
Wardlaw, W. See Bradley, D. C., 4916.
Webster, W., and Young, D. P., 4785.
Whetstone, J., 4841.
White, D. E. See Allsop, I. L., 4868.
Whiting, M. C. See Jones, E. R. H., 4765, and Mansfield, G. H., 4761.
Wiggins, L. F., and Wise, W. S., 4780.
Wiles, L. A., and Thomas, L. C., 4811.
Willix, R. L. S. See Allsop, I. L., 4868.
Winter, R. W. See Valentine, L., 4768.
Wise, W. S. See Wiggins, L. F., 4780.
Woods, B. M. See Hough, L., 4799.
Woods, R. J. See Johns, R. B., 4715.
Wrench, E. See Baddeley, G., 4943.
Yajima, H. See Ikeda, T., 4749.
Yeddanapalli, L. M., and Gnanapragasam, N. S., 4934.
Young, D. P. See Webster, W., 4785.
Zauli, C. See Mangini, A., 4960.

A brochure describing the activities of the Society and forms of application for Fellowship can be obtained from The General Secretary, The Chemical Society, Burlington House, Piccadilly, London, W.1.

Authors are requested to see that their papers conform as nearly as possible to the normal conventions of the *Journal* and should consult the brochure entitled "The Presentation of Papers for the *Journal* of the Chemical Society," which may be obtained from the General Secretary.

Attention is also drawn to changes in the method of quoting references (cf. *Proceedings*, July, 1955, 79).

918. *Co-ordination Compounds between Ethylenediaminetetra-acetic Acid and Gallium, Indium, and Thallium.*

By Kazuo Saito and (the late) Henry Terrey.

Co-ordination compounds of gallium, indium, tervalent thallium, and aluminium have been prepared crystalline, and their compositions determined. The solids contain one mol. of co-ordinated water. Potentiometric titration of their aqueous solutions with alkali hydroxide gives curves similar to that given by tervalent chromium or iron, showing that the co-ordinated water is capable of dissociating to a hydrogen ion and a hydroxy-complex anion. Under certain conditions, the co-ordinated water can be replaced by other donors including halogen or ammonia. Thus elements of Group IIIB form compounds with ethylenediaminetetra-acetic acid similar to those of aluminium, tervalent chromium, or ferric iron rather than to those of the rare-earth elements.

Schwarzenbach and Biedermann [1] suggested, from results of potentiometric titration, that anionic complexes are formed between ethylenediamine-*NNN'N'*-tetra-acetic acid [2] (EDTA) and aluminium, chromium, and ferric iron in a 1 : 1 molar ratio and contain 1 mol. of co-ordinated water, which dissociates at pH 5—9 to give a hydrogen ion and a hydroxy-complex ion ($M^{III}Y{\cdot}OH)^{2-}$ (Y = the EDTA radical, $C_{10}H_{12}O_8N_2^{4-}$). They further prepared a crystalline complex compound $HCrY,H_2O$ which did not lose its water on prolonged heating at 110° *in vacuo*.

Tervalent cobalt forms a similar anionic complex;[3] the co-ordinated water can be replaced by other donors, including halogens. The aquo-complex is, however, not stable enough to be obtained crystalline. Tervalent ions of the rare-earth elements, on the contrary, do not form such aquo-complex anions, although complex anions which contain other acid radicals are known.[4]

Little information was available concerning complex formation between EDTA and the tervalent metals of the gallium group. Flaschka and his co-worker [5] used the EDTA complexes of indium and tervalent thallium in the analysis of both elements, tacitly assuming the formation of 1 : 1 compounds. Schwarzenbach, Gut, and Anderegg,[6] in their extensive study on the stability constants of EDTA complexes with a variety of metal ions, gave the formation constants for the indium and the gallium complexes but did not state the composition of these complexes.

The present authors were of the opinion that the behaviour of tervalent ions of the gallium group towards EDTA could be compared with that of aluminium and of the rare-earth elements, since their ionic radii are between those of aluminium and the rare earths and their ionisation potentials are of comparable order. The complex compounds of gallium, indium, tervalent thallium, and aluminium with EDTA have therefore been prepared crystalline and their properties examined.

Experimental

Complex Compounds of Gallium.—Gallium nitrate, dissolved in water, was treated with an equivalent amount of disodium salt of EDTA and made strongly acidic with perchloric acid. *Monohydrogen aquoethylenediaminetetra-acetatogallium*(III) crystallised in a good yield on the addition of acetone (Found: Ga, 18·5; C, 31·8; total H, 4·0; loss at 110°, 0·2.

[1] Schwarzenbach and Biedermann, *Helv. Chim. Acta*, 1948, **31**, 459.
[2] Brintzinger and Hesse, *Z. anorg. Chem.*, 1942, **249**, 113; Brintzinger, Thiele, and Miller, *ibid.*, 1943, **251**, 285.
[3] Schwarzenbach, *Helv. Chim. Acta*, 1949, **32**, 839.
[4] Marsh, *J.*, 1950, 1819; Vickery, *J.*, 1951, 1817.
[5] Flaschka, *Mikrochem. Mikrochim. Acta*, 1952, **40**, 42; Flaschka and Amin, *Z. analyt. Chem.*, 1953, **140**, 6.
[6] Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937; Schwarzenbach and Freitag, *ibid.*, 1951, **34**, 1503.

$HGaC_{10}H_{14}O_9N_2$ requires Ga, 18·5; C, 31·9; H, 4·0; H_2O, 0%). The aqueous solution of this compound was neutralised with sodium or potassium hydroxide, kept in a vacuum-desiccator until small crystals were formed on the surface, then treated with acetone to precipitate the tetrahydrated *sodium* or dihydrated *potassium aquoethylenediaminetetra-acetatogallium* as prisms (Found: Ga, 15·1; Na, 5·0; C, 26·6; total H, 4·7; loss at 110°, 15·7. $NaGaC_{10}H_{14}O_9N_2.4H_2O$ requires Ga, 14·8; Na, 4·9; C, 25·5; H, 4·6; $4H_2O$, 15·3%. Found: Ga, 15·6; K, 9·0; C, 27·9; total H, 3·8; loss at 110°, 8·2. $KGaC_{10}H_{14}O_9N_2.2H_2O$ requires Ga, 15·5; K, 8·7; C, 26·6; H, 4·0; $2H_2O$, 8·0%). The water of crystallisation of both alkali salts was lost at 110°, but the co-ordinated water not until 250° where the decomposition of the organic component began.

Complex Compounds of Indium.—Freshly precipitated indium hydroxide, free from electrolytes, was boiled with an equivalent amount of EDTA until an almost clear solution was obtained. The mixture was filtered, made acid with perchloric acid, and treated with acetone. Colourless *monohydrogen aquoethylenediaminetetra-acetatoindium*(III) was precipitated; it was washed with acetone and dried between filter paper (Found: In, 27·1; C, 29·1; total H, 4·0; loss at 200°, 4·9. $HInC_{10}H_{14}O_9N_4$ requires In, 27·3; C, 28·5; H, 3·6; H_2O, 4·3%). When equivalent amounts of indium hydroxide, EDTA, and alkali hydroxide were boiled, reaction was faster. Filtration, evaporation, and treatment with acetone gave the dihydrated *sodium* or monohydrated *potassium aquoethylenediaminetetra-acetatoindium* (Found: In, 24·2; Na, 4·9; C, 25·1; total H, 3·8; loss at 110°, 7·5; further loss at 200°, 3·8. $NaInC_{10}H_{14}O_9N_4.2H_2O$ requires In, 23·9; Na, 5·0; C, 25·0; H, 3·8; $2H_2O$, 7·5; H_2O, 3·8%. Found: In, 24·2; K, 7·75; C, 24·9; total H, 3·7; loss at 200°, 7·75. $KInC_{10}H_{14}O_9N_4.H_2O$ requires In, 24·0; K, 8·2; C, 25·1; H, 3·35; $H_2O + H_2O$, 7·55%). The *ammonium salt monohydrate* is obtained when the monohydrogen complex is treated successively with aqueous ammonia (1 equiv.) and acetone (an excess of ammonia should be avoided; otherwise the salt would be contaminated by the ammine complex) (Found: In, 25·4; NH_3, 3·2; loss at 110°, 0·15; further loss at 200°, 8·3. $NH_4InC_{10}H_{14}O_9N_3.H_2O$ requires In, 25·1; NH_3, 3·7; $H_2O + H_2O$, 7·9%). The *cæsium salt trihydrate* is similarly obtained (Found: In, 18·8; Cs, 20·2; C, 19·8; total H, 3·7; loss at 110°, 11·8. $CsInC_{10}H_{14}O_9N_2.3H_2O$ requires In, 18·2; Cs, 21·9; C, 19·8; H, 3·3; $H_2O + 3H_2O$, 12·0%).

When the sodium salt of the aquo-complex was dissolved in a warm solution of sodium bromide (45%) and set aside for a few days, prisms of *disodium bromoethylenediaminetetra-acetatoindium*(III) *tetrahydrate* were precipitated. They were washed with water–acetone saturated with sodium bromide and then with acetone (Found: In, 19·2; Na, 7·9; Br, 13·1; loss at 110°, 13·1. $Na_2InC_{10}H_{13}O_8N_2Br.4H_2O$ requires In, 19·1; Na, 7·65; Br, 13·3; $4H_2O$, 12·0%). *Diammonium chloroethylenediaminetetra-acetatoindium*(III) *dihydrate* was obtained in cubes by boiling equivalent amounts of indium hydroxide and EDTA in a concentrated solution of ammonium chloride, made basic with ammonia [Found: In, 22·8; NH_3, 6·7; Cl, 6·5; loss at 110°, 7·1. $(NH_4)_2InC_{10}H_{13}O_8N_2Cl.2H_2O$ requires In, 22·5; NH_3, 6·95; Cl, 6·7; $2H_2O$, 7·1%]. Plates of *ammonium amminoethylenediaminetetra-acetatoindium*(III) *monohydrate* were precipitated on treatment of a solution of the ammonium salt of the aquo-complex in aqueous ammonia with acetone [Found: In, 25·2; loss at 105°, 4·3; NH_3, 7·5. $NH_4InC_{10}H_{12}O_8N_2NH_3.H_2O$ requires In, 25·2; NH_3, 7·5; H_2O, 3·95%]. All of these halogeno- and ammino-complexes are soluble in water and rapidly hydrolysed to the aquo-complex anion $(InY{\cdot}H_2O)^-$ and bromide, chloride, or ammonium ions. The water of crystallisation of these compounds is removed at 110°.

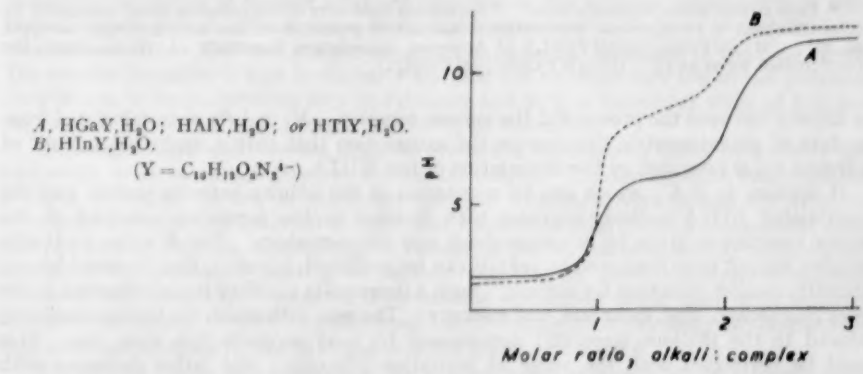
Complex Compound of Tervalent Thallium.—Metallic thallium was dissolved in concentrated nitric acid and oxidised with chlorine. The product was treated with aqueous ammonia, yielding a dark brown precipitate of the hydroxide, which was dissolved in nitric acid. Aqueous solution of the equivalent amount of disodium salt of EDTA was gradually added with stirring. Colourless *monohydrogen aquoethylenediaminetetra-acetatothallium*(III) was precipitated on the addition of acetone (Found: Tl, 39·6; C, 24·3; H, 3·3. $HTlC_{10}H_{14}O_9N_2$ requires Tl, 40·0; C, 23·5; H, 3·0%). This began to char at about 95° and gradually lost weight until complete decomposition of the organic residue occurred.

Complex Compounds of Aluminium.—Freshly precipitated aluminium hydroxide was boiled with an equivalent amount of EDTA until a clear solution was obtained, which was filtered, evaporated, and treated with ethanol to precipitate prisms of *monohydrogen aquoethylenediaminetetra-acetatoaluminium*(III) (Found: Al, 8·2; C, 36·6; H, 5·1. $HAlC_{10}H_{14}O_9N_2$ requires Al, 8·1; C, 36·0; H, 4·5%). An aqueous solution of this compound was exactly neutralised, kept in a vacuum-desiccator until crystals were formed, and treated with acetone

to precipitate prisms of *sodium aquoethylenediaminetetra-acetatoaluminium*(III) *tetrahydrate* or the *potassium salt dihydrate* (Found : Al, 6·40; Na, 5·9; C, 29·7; total H, 5·1; loss at 110°, 16·5. $NaAlC_{10}H_{14}O_9N_2.4H_2O$ requires Al, 6·3; Na, 5·4; C, 28·1; H, 5·2; $4H_2O$, 16·8%. Found : Al, 6·8; K, 8·5; C, 31·7; total H, 4·3; loss at 110°, 9·0. $KAlC_{10}H_{14}O_9N_2.2H_2O$ requires Al, 6·6; K, 9·6; C, 29·4; H, 4·4; $2H_2O$, 8·8%). Satisfactory values for carbon were obtained with the anhydrous *aquo-salts* (Found : C, 34·1. $NaAlC_{10}H_{14}O_9N_2$ requires C, 33·7%. Found : C, 32·5. $KAlC_{10}H_{14}O_9N_2$ requires C, 32·3%).

The monohydrogen complexes of these metals are sparingly soluble in water whilst the salts are very soluble but not hygroscopic. None of them is soluble in organic solvents, including those having higher dielectric constants. Aqueous solutions of anionic complexes of gallium, indium, and aluminium fail to show ordinary reactions of the metal ions. On the addition of a concentrated solution of alkali hydroxide, however, the indium complex gives a colourless precipitate of the hydroxide. An aqueous solution of the thallic complex appears to be less stable towards reagents. On the addition of alkali hydroxide the brown hydroxide is precipitated. It oxidises potassium iodide to iodine equivalent in amount to the thallium. No significant reduction is observed, however, on the treatment with sulphur dioxide.

Potentiometric Titration.—Potentiometric titration curves of the aqueous solution of the monohydrogen complexes of gallium, indium, thallium, amd aluminium with alkali hydroxide, followed by the use of a glass electrode, are shown in the Figure. Similar curves were obtained



at a constant ionic strength in 0·1M-potassium nitrate. The curves for the alkali salts are respectively identical with the second half of those in the Figure, regardless of the cationic component of the complex salts. The solution of sodium bromo-EDTA-indium(III) gives a curve identical with that of the aquo-complex, whilst curves of ammonium salts of aquo-, chloro- and ammino-EDTA complexes are less distinctive.

Absorption Spectra.—Aqueous solution of the complexes of gallium, indium, and aluminium are non-absorbing in the range 950—220 mμ (absorption of EDTA itself starts at 220 mμ); the absorption of the thallic complex remarkably increases below 320 mμ. Generally it is believed that the greater the stability of a chelate compound, the shorter the wavelength at which the characteristic absorption cuts off.

Analysis.—For analysis of metallic components of the complex compounds, the sample was decomposed with sulphuric and nitric acid. The hydroxides of gallium, indium, and aluminium were precipitated from acid solution with aqueous ammonia and ignited to oxides. Tervalent thallium was reduced to the univalent state with sulphur dioxide and precipitated with chromate ions in ammoniacal solution. Alkalis were determined in the filtrate from the hydroxides by the usual method. Bromide and chloride were precipitated with a known amount of silver nitrate; the excess of the latter was back-titrated with potassium thiocyanate (iron alum as indicator). Ammonia was determined by the Kjeldahl method. Since the halogeno-complex anions are very rapidly hydrolysed in an aqueous solution, no special procedure was required for the displacement of halogens. The analyses of carbon and hydrogen were carried out mainly by Mr. A. V. Winter, whom the authors thank. They thank also Dr. Judith Grenville-Wells for her help in crystallographic measurement.

Discussion

From the titration curve it is seen that the anionic complexes of EDTA with gallium, indium, and thallium in aqueous solution contain one mol. of co-ordinated water, which as with chromium, ferric iron, and aluminium, dissociates to give a hydrogen ion. The fact that one mol. of water is removed with difficulty from the crystals of the complexes supports the view that it is held in the ligand also in the solid state. It was thus concluded that the co-ordination compounds of the gallium group of elements with EDTA are similar to those of aluminium (and of ferric iron and chromium) rather than to those of the rare-earth elements.

Since the formation of the complexes is extensive enough,[6] apparent values of dissociation constants for protons calculated as shown below could provide an approximation to

Comparison of EDTA *complexes of the Group* IIIB *elements.*

	Al	Ga	In	Tl
r (Å) [a]	0·57	0·62	0·92	1·05
K [b]	$1·3 \times 10^{16}$	$1·8 \times 10^{20}$	$8·9 \times 10^{24}$	—
K_1 [c]	$0·10 \times 10^{-3}$	$3·9 \times 10^{-6}$	$>1 \times 10^{-1}$	$0·20 \times 10^{-3}$
K_2 [d]	$0·69 \times 10^{-4}$	$1·2 \times 10^{-4}$	$1·6 \times 10^{-9}$	$0·32 \times 10^{-4}$

[a] Ionic radius (from Pauling's table). [b] Formation constants of the complex anion (measured by Schwarzenbach [6]). [c] Apparent dissociation constants of proton from the monohydrogen complex at 15°: $[H^-][MY{\cdot}OH_2^-]/[HMY{\cdot}OH_2]$. [d] Apparent dissociation constants of proton from the co-ordinated water at 15°: $[H^-][MY{\cdot}OH^{2-}]/[MY{\cdot}OH_2^-]$.

the affinity between the proton and the anionic complex. K_1 and K_2 were calculated from the data of potentiometric titration on the assumption that only a negligible amount of hydrogen ion is provided by the dissociation of free EDTA.

It appears as if K_1, which can be a criterion of the affinity between proton and the co-ordinated EDTA radical, increases with increase in the formation constant of the anionic complex as given by Schwarzenbach and his co-workers. The K value for thallic complex has not been measured as yet; it can be predicted, however, that it would be significantly smaller than that for indium. Such a decrease in stability is also observed in the series magnesium, zinc, cadmium, and mercury. The ease with which the thallic complex is reduced to the thallous state and decomposed by heat supports this view, too. This could be correlated with the value of ionisation potential; the latter decreases with increasing ionic radius in a sub-group of the Periodic Table, but mercury and thallium have greater values than those of cadmium and indium, respectively.

The K_2 values appear to decrease with increase in the ionic radius. The smaller the ionic radius, the stronger the interaction between the metal ion and the co-ordinated water. The electron cloud of the oxygen atom might be so attracted by the metal ion that the electrolytic dissociation of proton is promoted to give a greater K_2 value. This also accounts for the loose combination of water in the indium complex. The heaviest member of the sub-group again shows an irregular behaviour.

The fact that the monohydrogen complexes of gallium and aluminium and their sodium and potassium salts have respectively the same numbers of water molecules of crystallisation suggests that they may form isomorphous crystals. A comparison by the Debye–Scherrer method disclosed that they formed very similar crystals although it was not certain that they were isomorphous.

One of the authors (K. S.) thanks the Ramsay Memorial Fellowships Trust for the award of a fellowship and Professor C. K. Ingold, Professor R. S. Nyholm, and Dr. J. E. Salmon for valuable discussions.

William Ramsay and Ralph Forster Laboratories, University College, London, W.C.1.
[Present address (K. S.): Institute for Nuclear Study, The University of Tokyo, Tanashi P.O., Tokyo, Japan.]
[*Received, December 6th*, 1955.]

919. *Observations on Ammonium Ferric Disulphate Dodecahydrate (Ammonium Ferric Alum) and Some of its Derivatives.*

By Henry Bassett.

Ammonium ferric alum effloresces to yield $NH_4Fe(SO_4)_2.2H_2O$ or $NH_4Fe(SO_4)_2$ under dry tropical conditions. The preparation of a new basic double salt is described; its relation to the ammonium and potassium basic ferric sulphates first prepared in 1827 is discussed.

Some evidence is given for the replacement of ammonium by hydroxonium and of $(SO_4)^{2-}$ by $[(OH)_2(H_2O)_2]^{2-}$ in such salts, and even in the alum. The various colours of ferric alum are explained in a new way.

Ammonium ferric alum is metastable under the dry tropical conditions of central Tanganyika and gradually loses water to yield a white powder consisting of $NH_4Fe(SO_4)_2$ in the form of plates belonging to the hexagonal system. These are relatively large (diameter 0·1—0·2 mm.) because fluctuations in atmospheric humidity permit the occasional formation of films of adsorbed moisture on the primary efflorescence in which crystal growth occurs. The average shade day temperature at Dodoma is near 22° with a maximum of 27·8—33·2° and a night minimum of 10·2—18° according to the time of year. The relative humidity is high in the early morning but becomes very low in the afternoon. At 8·30 a.m. it ranges between 88% in February and 64% in November while at 2·30 p.m. the range is between 57% in February and 27% in November.[1]

Unchanged alum was removed from the product of efflorescence either by leaching with cold water, or by continued exposure to constant weight. The final product then contained 2—2½% of water. A few of the larger purplish fragments were picked out from the effloresced material and analysed to show that the second solid phase was unaltered alum. Anhydrous $NH_4Fe(SO_4)_2$, crystallising in hexagonal plates, was prepared by Lachaud and Lepièrre [2] by prolonged heating of ferrous sulphate in fused ammonium sulphate. Weinland and Ensgraber [3] obtained it by heating ammonium ferric alum with sulphuric acid for some hours. Vegard and Maurstad [4] showed that the *X*-ray diagram corresponded with a hexagonal space lattice having $a = 4·825$ Å and $c = 8·310$ Å.

Wiedemann [5] says that ammonium ferric alum melts at about 34° to a brown liquid which does not solidify completely on cooling. Erdmann and Köthner [6] give the m. p. as 43—44°, Locke [7] as 40°, Houda and Ishiwara [8] as 37°, and Ephraim and Wagner [9] state that the salt becomes brown at about 33° and is completely melted at 41°.

It seems clear from the careful observations of Welo [10] that ammonium ferric alum has no congruent m. p. but that there is an incongruent m. p. at approximately 37° at which transition occurs from the solid alum to a new solid phase and saturated solution. This indicates that the alum is relatively unstable towards either a lower hydrate or the anhydrous salt. Welo did not determine the nature of the new solid phase which is formed at about 37°.

Crystals of $NH_4Fe(SO_4)_2$ when kept wet at about 25° regenerate the alum after many days. If attempts are made to hasten the process by heating with water, insoluble yellow basic salts are formed. Their formation could explain Lupton's [11] statement that the

[1] "Summary of Meteorological Observations for 1949," East African Meteorological Department.
[2] Lachaud and Lepièrre, *Bull. Soc. chim.*, 1892, **7**, 356.
[3] Weinland and Ensgraber, *Z. anorg. Chem.*, 1913, **84**, 340.
[4] Vegard and Maurstad, *Z. Kryst.*, 1929, **69**, 519.
[5] Wiedemann, *Wied. Ann.*, 1882, **17**, 569.
[6] Erdmann and Köthner, *Annalen*, 1897, **294**, 2.
[7] Locke, *Amer. Chem. J.*, 1901, **26**, 166.
[8] Houda and Ishiwara, *Sci. Reports Tôhoku Univ.* 1915, **4**, 231.
[9] Ephraim and Wagner, *Ber.*, 1919, **50**, 1105.
[10] Welo, *Nature*, 1929, **124**, 575.
[11] Lupton, *J.*, 1875, **28**, 201.

alum lost 23 out of 24 molecules water at 150° and all at 230°. Somewhat similar statements are made by Adolphs [12] and Masson.[13] The alum would melt partially at about 37° and basic salts would separate from the solution so formed on further heating; a fairly high temperature is required to drive off all water from these basic salts.

The dark solution and the yellow basic salt obtained on warming the anhydrous salt with water were separated by decantation. The yellow solid was dissolved by addition of sulphuric acid. The combined filtered solutions after standing at room temperature for some months yielded pale violet tetragonal bipyramids of $NH_4Fe(SO_4)_2,2H_2O$ *via* the white anhydrous $NH_4Fe(SO_4)$. The preparation and analysis of this compound have been described briefly by Taylor and Bassett.[14] The yellowish-brown solution produced by water and excess of $NH_4Fe(SO_4)_2$ was inoculated with the dihydrate. After a fortnight the original hexagonal plates of $NH_4Fe(SO_4)_2$ had all been converted into aggregates of minute needles of the dihydrate.

The conversion of the original alum into the dihydrate could also be accomplished by treating the solid with a little of the dihydrate. Observations made during these experiments confirmed the opinion that the process of dehydration was complex and involved crystal growth in surface films of solution which were sometimes clearly present. It seems clear from these results that both in absence of any excess of sulphuric acid and also with much of it present the stable sequence of changes is

$$NH_4Fe(SO_4)_2,12HO_2 \rightleftharpoons NH_4Fe(SO_4)_2,2H_2O \rightleftharpoons NH_4Fe(SO_4)_2$$

in the temperature range 25° to 30° though the metastable change

$$NH_4Fe(SO_4)_2,12H_2O \rightleftharpoons NH_4Fe(SO_4)_2$$

can also occur quite readily. No indications of any hydrates intermediate between the dodecahydrate and the dihydrate have been noticed.

When some of the mainly dehydrated alum was kept with a small proportion of water and shaken occasionally at room temperature (25°) for a few hours all the fragments of unaltered alum dissolved but some of the $NH_4Fe(SO_4)_2$ remained undissolved for a long time. The mixture was left to stand in the covered beaker and as evaporation proceeded beautiful yellowish brown hexagonal plates and prisms separated from the brownish solution which crept up the sides of the beaker. Their composition agrees very closely with that required for a basic salt $1{\cdot}5[(NH_4)_2O],Fe_2O_3,4SO_3,5{\cdot}5H_2O$. This dissolves readily in water at 25° to give a solution which is nearly colourless when dilute but yellowish brown when concentrated. It has not been recorded previously.

Maus,[15] by spontaneous evaporation of a solution of ammonium ferric alum to which ammonia had been added until the precipitate formed no longer dissolved, obtained crystals with composition very close to that required for $2(NH_4)_2O,Fe_2O_3,4SO_3,4H_2O$. A solution of potassium ferric alum treated in the same way with potassium hydroxide yielded crystals approximating to $2K_2O,Fe_2O_3,4SO_3,6H_2O$. Both of these preparations by Maus and the new one described above form precisely similar hexagonal plates and prisms which indicates some probable close relationship. Maus was of this opinion regarding his two salts but noticed that there was more discrepancy between the analytical and calculated figures for the potassium salt than for the ammonium one, the potassium content found by analysis being much too low.

By rewriting Maus's ammonium salt and the new salt as $(NH_4)_4,Fe_2O,(SO_4)_4,(H_2O)_4$ and $(NH_4)_3,(H_3O),Fe_2O,(SO_4)_4,(H_2O)_4$ the new salt is seen to be derived from Maus's salt by replacement of one quarter of the ammonium by hydroxonium.

The composition found by Maus for his potassium salt agrees closely with that calculated

[12] Adolphs, Dissertation, Heidelberg, 1904.
[13] Masson, *J.*, 1910, **97**, 862.
[14] Taylor and Bassett, *J.*, 1952, 4438.
[15] Maus, *Pogg. Ann.*, 1827, **11**, 78.

for a mixture of : 70% of $K_4Fe_2O(SO_4)_4(H_2O)_4$, 20% of $K_3(H_3O)Fe_2O(SO_4)_4(H_2O)_4$, and 10% of $K_3(H_3O)Fe_2O(SO_4)_3[(OH)_2(H_2O)_2](H_2O)_4$.

Justification for postulating small replacement of $[SO_4]^{2-}$ by $[(OH)_2(H_2O)_2]^{2-}$ is derived from the replacement of $(SiO_4)^{4-}$ by $[(OH)_4]^{4-}$ which can occur in silicates. The most striking example of this is found in the garnet group.[16]

Such replacement of $(SO_4)^{2-}$ may well occur to a limited extent in many cases and could explain the small deficiency of sulphate in the fresh supply of ferric alum and in the $NH_4Fe(SO_4)_2$ derived from the old supply.

Partial replacement of ammonium by oxonium probably occurs much more frequently than is realised. It has been shown [17] that $H_2SO_4.Al_2(SO_4)_3.2H_2O$ and $NH_4Fe(SO_4)_2$ are isomorphous and that the former is the hydroxonium salt $(H_3O)Al(SO_4)_2$. Shishkin [18] has shown that replacement of oxonium by ammonium ions can link together structurally similar basic, neutral, and acid salts.

The existence of colourless and yellow varieties of ammonium ferric alum is explicable in terms of small amounts of yellow $[FeOH(H_2O)_5]^{2+}$ ions replacing $[Fe(H_2O)_6]^{3+}$ octahedra [19] of the alum lattice and balanced by replacement of $(SO_4)^{2-}$ by $[OH(H_2O)_3]^{-}$. If the proportion of $[FeOH(H_2O)_5]^{2+}$ were just right optical bleaching of the violet colour of the pure alum would occur. With more of the yellow ion a yellow alum would result. Ostwald [20] and Perman [21] attributed a similar rôle to colloidal ferric hydroxide but this seems less probable.

Experimental

Analysis.—No manganese was detected by the periodate test in any of the samples used. Iron was precipitated twice with aqueous ammonia solution; a third precipitation was found unnecessary. After ignition, ferric oxide was dissolved in concentrated hydrochloric acid, and its weight corrected for the silica present : dissolved silica in aqueous ammonia is a serious analytical nuisance in tropical conditions. Sulphate was precipitated from acidified solution as barium sulphate, and weighed. Water was estimated by difference.

Product of Efflorescence.—(*a*) A sample (4·4 g.) was treated for 1 hr. with water at 25° with occasional shaking. The residue was filtered off, washed with alcohol, and dried in air (yield 2·8 g.) [Found : $(NH_4)_2O$, 8·8; Fe_2O_3, 30·2; SO_3, 59·0; H_2O, 2·0. Calc. for $NH_4Fe(SO_4)_2$: $(NH_4)_2O$, 9·77; Fe_2O_3, 30·04; SO_3, 60·19%]. (*b*) A sample (14 g.) was exposed in a shallow dish for four months (November to March) (loss 0·1 g.) [Found : $(NH_4)_2O$, 9·7; Fe_2O_3, 29·5; SO_3, 58·2; H_2O, 2·6%]. (*c*) A sample (1·6 g.) was exposed for 5 weeks (June and July) (loss 0·02 g.) [Found : $(NH_4)_2O$, 9·8; Fe_2O_3, 29·8; SO_3, 58·4; H_2O, 2·0%].

Hydration of Ammonium Ferric Disulphate.—(*a*) A sample of the mainly dehydrated alum was treated with water, a large amount of $NH_4Fe(SO_4)_2$ remaining undissolved. On heating it was converted into a yellow basic salt, which, after decantation of the dark solution, was dissolved in the minimum of sulphuric acid. The two solutions were mixed, filtered into a silica dish, and allowed to evaporate at 25—30°. After a few weeks crystals of alum appeared, and in a few more weeks this was converted into white anhydrous $NH_4Fe(SO_4)_2$ which in another four weeks formed pale violet prisms of the dihydrate,[14] soluble with long shaking in 1·7M-hydrochloric acid at 25—30°.

(*b*) Water and excess of the anhydrous disulphate in a stoppered bottle at 25° slowly formed a yellow-brown solution. After a few days this was inoculated with a little dihydrate, and after two weeks the whole had been converted into dihydrate, except for a few large (diameter 1 cm.) crystals of alum.

Conversion of Dodecahydrate into Dihydrate.—A lump of fresh alum, splinters of which were shown to contain no doubly-refracting material [Found : $(NH_4)_2O$, 5·5; Fe_2O_3, 16·6; SO_3, 32·7; H_2O, 45·2. Calc. for $NH_4Fe(SO_4)_2.12H_2O$: $(NH_4)_2O$, 5·4; Fe_2O_3, 16·6; SO_3, 33·2; H_2O, 44·8%], was sprinkled with a little dihydrate and left under a small inverted beaker from July

[16] Winchell, "Elements of Optical Mineralogy," John Wiley, New York, 5th edn., 1951, Part II, p. 483.
[17] Taylor and Bassett, *J.*, 1952, **4439**.
[18] Shishkin, *Zapiski Vsesoyuz Mineral Obshchestva* (*Mém. Soc. russe minéral.*), 1950, **79**, 94—102; *Chem. Abs.*, 1950, **44**, 7612; *Zhur. obshchei Khim.*, 1951, **21**, 456—467; *Chem. Abs.*, 1951, **45**, 6115.
[19] Lipson and Beevers, *Proc. Roy. Soc.*, 1935, *A*, **148**, 664.
[20] Ostwald, "Grundlinien der anorg. Chem.," Leipzig, 1900, p. 585.
[21] Perman, *J.*, 1921, **119**, 1996.

to January. It had become a thin violet shell of the original lump, composed of intergrown nodules of the dihydrate: inside was a mass of similar material stained yellow by a film of basic salt.

Preparation of a Basic Salt.—A sample of the mainly dehydrated alum was shaken with water for several hours at 25°. Unchanged alum dissolved quickly, the anhydrous salt only slowly. On standing and being allowed to evaporate, the mixture yielded yellow-brown hexagonal plates and prisms which were obtained practically free from mother-liquor by means of hardened filter-paper. They became stable in air after losing 2% of moisture {Found: NH_3, 7·5; Fe_2O_3, 24·4; SO_3, 49·0; H_2O, 19·1. $1{\cdot}5[(NH_4)_2O],Fe_2O_3,4SO_3,5\frac{1}{2}H_2O$ requires NH_3, 7·8; Fe_2O_3, 24·3; SO_3, 48·7; H_2O, 19·2%}. The basic *salt* dissolves readily in water at 25°.

The author thanks Mr. G. M. Stockley, late Director of the Survey, for facilities.

GEOLOGICAL SURVEY OF TANGANYIKA, DODOMA.
[*Present Address*: THE UNIVERSITY, READING.]

[*Received, April 26th*, 1956.]

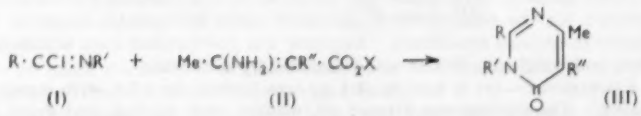
---

920. *A New Synthesis of 2 : 3 : 5 : 6-Substituted 4-Pyrimidones.*

By BENJAMIN STASKUN and HENRY STEPHEN.

2 : 3 : 5 : 6-Substituted 4-pyrimidones are readily synthesised by condensation of imidoyl chlorides with methyl or ethyl α-alkyl-β-aminocrotonates.

THE present synthesis involves condensation of imidoyl chlorides (I) with the amino-group of methyl or ethyl α-alkyl-β-aminocrotonates (II), followed by ring closure to 2 : 3 : 5 : 6-substituted 4-pyrimidones (III), the reaction being analogous to the synthesis of quin-



azolones from imidoyl chlorides and methyl anthranilate.[1] The methyl and the ethyl ester of the same α-alkyl-β-aminocrotonic acid give, of course, the same pyrimidone.

The synthesis was modified by preparing imidoyl chlorides by rearranging ketoximes with phosphorus pentachloride,[2] which has the advantage that certain imidoyl chlorides, *e.g.*, Me·CCl:NPh, which are difficult to prepare from the amides, can be obtained and used *in situ*, and it is unnecessary to remove the phosphorus oxychloride produced during the rearrangement since it has no action on α-alkyl-β-aminocrotonic esters under the experimental conditions. Since hydrogen chloride and methanol or ethanol produced during the condensations react with imidoyl chlorides and α-alkyl-β-aminocrotonic esters the yields of pyrimidones were 50—65% when equimolecular proportions of the reactants were used. Improved yields (70—80%) were obtained by using an excess of either imidoyl chloride or ester.

EXPERIMENTAL

α-Alkyl-β-aminocrotonic esters were prepared by Conrad and Epstein's method,[3] and stored over phosphoric oxide.

General Procedures (cf. Table 1).—(*a*) The imidoyl chloride (0·01 mol.) and α-alkyl-β-aminocrotonic ester (0·005, 0·01, or 0·02 mol.) were refluxed in dry chloroform (40 c.c.) for 3—4 hr. (method A) or allowed to remain at room temperature for 2—3 days (method B). These methods furnish pyrimidones in poor yields from relatively unreactive imidoyl chlorides. In such cases the imidoyl chloride and ester were heated (paraffin-bath) in the absence of a solvent (method C), hydrogen chloride and alcohol being evolved. The products (any of the methods) were acidified with dilute hydrochloric acid and steam-distilled; this hydrolysed unchanged ester to give steam-volatile or water-soluble products, and converted unchanged imidoyl chloride

[1] Levy and Stephen, *J.*, 1956, 985.
[2] Stephen and Staskun, *J.*, 1956, 980.
[3] Conrad and Epstein, *Ber.*, 1887, **20**, 3055.

TABLE 1. 2 : 3 : 5 : 6-*Substituted pyrimidones.*

R·CCl:NR′		Me·C(NH$_2$):CR″·CO$_2$X				Product				
R	R′	R″	X	Molar ratio (I) : (II)	Method	Formula	Yield (%)	M. p.	Found, N (%)	Reqd., N (%)
Ph	Ph	Me	Me	1 : 1	C, 140°, ½ hr.	—	—	—	—	—
		Me	Et	1 : 1	C, 140°, ½ hr.	$C_{18}H_{16}ON_2$	45	157°	10·35	10·15
		Et	Et	1 : 2	A, 4 hr.	$C_{19}H_{18}ON_2$	79	159	9·6	9·65
Ph	o-C_6H_4Me	Me	Me	1 : 1	A, 3 hr.	$C_{19}H_{18}ON_2$	53	114	9·6	9·65
		Et	Et	1 : 2	A, 4 hr.	$C_{20}H_{20}ON_2$	80	152	9·2	9·3
Ph	m-C_6H_4Me	Me	Me	1 : 1	C, 100°, ½ hr.	$C_{19}H_{18}ON_2$	31	129	9·95	9·65
		Me	Et	1 : 1	C, 100°, ½ hr.	—	28	—	—	—
		Et	Me	1 : 1	C, 100°, ½ hr.	$C_{20}H_{20}ON_2$	77	136	9·4	9·2
		Et	Et	1 : 2	A, 3 hr.					
Ph	p-C_6H_4Me	Me	Me	1 : 2	A, 3 hr.	$C_{19}H_{18}ON_2$	77	146	9·7	9·65
		Et	Et	1 : 2	B, 3 hr.	$C_{20}H_{20}ON_2$	75	152	9·2	9·2
Ph	2 : 4 : 1-$Me_2C_6H_3$	Me	Me	2 : 1	A, 3 hr.	$C_{20}H_{20}ON_2$	83	152	9·1	9·2
		Me	Et	2 : 1	A, 3 hr.	—	—	—	—	—
		Et	Et	2 : 1	A, 3 hr.	$C_{21}H_{22}ON_2$	83	146	8·6	8·8
Ph	p-MeO·C_6H_4	Et	Et	1 : 2	B, 3 hr.	$C_{20}H_{20}O_2N_2$	81	161	8·75	8·75
		Pr^n	Me	1 : 2	C, 155°, ½ hr.	$C_{21}H_{22}O_2N_2$	55	163	8·3	8·4
Ph	m-NO_2·C_6H_4	Me	Me	1 : 2	C, 140°, ½ hr.	$C_{18}H_{13}O_3N_3$	62	159	13·3	13·1
		Me	Et	1 : 2	C, 140°, ½ hr.	—	34	—	—	—
		Et	Me	1 : 2	C, 140°, ½ hr.	$C_{19}H_{17}O_3N_3$	24	160	12·35	12·5
		Et	Et	1 : 2	C, 140°, ½ hr.	—	38	—	—	—
Ph	1-$C_{10}H_7$	Me	Et	1 : 2	A, 3 hr.	$C_{22}H_{18}ON_2$	64	174	8·2	8·6
Ph	2-$C_{10}H_7$	Me	Et	1 : 2	A, 3 hr.	$C_{22}H_{18}ON_2$	50	189	8·4	8·6
		Et	Et	1 : 2	A, 3 hr.	$C_{23}H_{20}ON_2$	40	184	8·5	8·2
Ph	o-C_6H_4Cl	Me	Et	2 : 1	A, 3 hr.	$C_{19}H_{15}ON_2Cl$	13	151	9·2	9·0
		Et	Et	2 : 1	C, 170°, ½ hr.	$C_{19}H_{17}ON_2Cl$	32	192	8·4	8·6
Ph	m-C_6H_4Cl	Me	Me	1 : 1	C, 150°, ½ hr.	$C_{18}H_{13}ON_2Cl$	35	152	9·0	9·0
Ph	p-C_6H_4Cl	Et	Et	1 : 2	C, 185°, ½ hr.	$C_{19}H_{17}ON_2Cl$	59	148	8·4	8·6
		Pr^n	Me	1 : 2	C, 185°, ½ hr.	$C_{20}H_{19}ON_2Cl$	37	154	8·05	8·2
Ph	Et	Et	Et	1 : 2	B, 3 hr.	$C_{14}H_{16}ON_2$	73	82	12·5	12·3
		Me	Et	1 : 2	B, 3 hr.	$C_{13}H_{14}ON_2$	51	118	11·25	11·5
o-C_6H_4Me	Ph	Me	Me	2 : 1	A, 3 hr.	$C_{19}H_{18}ON_2$	80	112	9·45	9·65
		Et	Et	2 : 1	A, 3 hr.	$C_{20}H_{20}ON_2$	74	137	9·1	9·2
p-C_6H_4Cl	Ph	Et	Et	1 : 2	C, 155°, ½ hr.	$C_{19}H_{17}ON_2Cl$	67	146	8·8	8·6
		Pr^n	Me	1 : 2	C, 155°, ½ hr.	$C_{20}H_{19}ON_2Cl$	21	151	8·3	8·3
3 : 4 : 5-$(MeO)_3C_6H_2$	Ph	Me	Me	1 : 2	A, 3 hr.	$C_{21}H_{22}O_4N_2$	20	181	8·0	7·65
		Et	Et	1 : 2	A, 3 hr.	$C_{22}H_{24}O_4N_2$	37	129	7·2	7·4

into the amide. After cooling, the latter was filtered off, and the filtrate, on treatment with charcoal and ammonia, deposited the crude pyrimidone which crystallised from dilute methanol or ethanol in colourless needles.

(*b*) To a solution of the ketoxime (0·01 mol.) in chloroform (50 c.c.) at 0° finely powdered phosphorus pentachloride (0·01 mol.) was rapidly added and the whole shaken for 1—2 min. to dissolve the pentachloride. The solution was removed from the ice-bath and treated according to one of the following procedures. The solution was refluxed for 15 min. to complete the rearrangement of the ketoxime, the α-alkyl-β-aminocrotonic ester (0·02—0·03 mol.) in chloroform (10 c.c.) was added, and refluxing continued for 2—3 hr. (method D). Alternatively, the solution after remaining at room temperature for 2 hr. was cooled (10°), the ester (0·02—

TABLE 2.

			Pyrimidone			
Ketoxime	R in $Me{\cdot}C(NH_2){:}CR{\cdot}CO_2X$	Method	Formula	Yield (%)	M. p.	Found, N (%)	Reqd., N (%)
PhMeC:N·OH	Et	E	$C_{14}H_{16}ON_2$	65	126°	12·5	12·3
(*p*-C_6H_4Me)MeC:N·OH	Et	E	$C_{15}H_{18}ON_2$	65	82	11·6	11·6
"	Me	D	$C_{14}H_{16}ON_2$	65	146	12·2	12·3
2-$C_{10}H_7{\cdot}CMe$:N·OH ...	Et	F	$C_{15}H_{18}ON_2,HCl$	65	130	8·4	8·9
PhPr^{n}C:N·OH	Et	E	$C_{15}H_{18}ON_2$	72	106	11·3	11·6
"	Me	E	$C_{14}H_{16}ON_2$	35	73	12·1	12·3
(*p*-$C_6H_4Me)_2C$:N·OH...	Me	F	$C_{30}H_{36}ON_2$	73	128	9·5	9·2
" ...	Et	F	$C_{31}H_{32}ON_2$	60	140	9·0	8·8
Ph_2C:N·OH	Et	D	Table 1	55	157	—	—

0·03 mol.) in chloroform (10 c.c.; 10°) was added, and the mixture allowed to remain for 1—2 days at room temperature (method E).

The following method (F) gave good yields of pyrimidones. The rearranged solution of the ketoxime, after remaining for 2 hr. at room temperature, was distilled at 40—45°/30 mm. to remove solvent (30 c.c.) and some phosphorus oxychloride. The α-alkyl-β-aminocrotonic ester (0·02—0·03 mol.) in chloroform (30 c.c.) was added and the mixture stored for 1—2 days at room temperature. The products were treated as described previously. Results are recorded in Table 2. The pyrimidones crystallised in colourless needles from methanol or ethanol.

UNIVERSITY OF THE WITWATERSRAND,
JOHANNESBURG, SOUTH AFRICA.

[*Received, June 5th*, 1956.]

921. *Structure and Reactivity of the Oxy-anions of Transition Metals. Part II.* Investigations by Electron-spin Resonance.*

By A. CARRINGTON, D. J. E. INGRAM, D. SCHONLAND, and M. C. R. SYMONS.

Electron-spin resonance absorption spectra are reported for certain tetrahedral oxy-anions of manganese, iron, chromium, ruthenium, and rhenium containing either one or two unpaired electrons. The results are discussed in terms of an orbital level scheme recently proposed by Wolfsberg and Helmholz [1] for the ions MnO_4^{--}, CrO_4^{3-}, and ClO_4^{--}.

ONE of the most direct applications of electron-spin resonance is to compounds of the transition-group elements where the unpaired electrons are located largely in the inner shells of the particular atoms concerned. A study of their characteristics will thus give considerable information about the valency and energy state of the paramagnetic atom together with details of the bonding to its nearest neighbours. Examples of this type of work are the measurements on different ferric compounds to show the transition from ionic to covalent bonding,[2,3] and the results obtained from the chloroiridate ion [4] and

* Part I, *J.*, 1956, 3373.

[1] Wolfsberg and Helmholz, *J. Chem. Phys.*, 1952, **20**, 837.
[2] Bagguley, Bleaney, Griffiths, Penrose, and Plumpton, *Proc. Phys. Soc.*, 1948, **61**, 542.
[3] Bleaney and Ingram, *ibid.*, 1952, **65**, 953.
[4] Griffiths and Owen, *Proc. Roy. Soc.*, 1954, *A*, **226**, 96.

similar compounds, where the amount of electron-transfer and π-bond character can be accurately calculated.

A study of the oxy-anions of the transition-group elements might therefore throw additional light on their oxidation states and chemical bonding. These systems are not always the best to study by electron-resonance techniques since the compounds are usually stable only in concentrated alkaline solution and often can only be obtained easily in an alkali glass or in an amorphous form. Hence all the additional information available from angular variation in a single crystal is not readily obtained. Nevertheless, the variation of resonant absorption with temperature, and the effective spin value of the ground state can be used to give some information on the likely oxidation state and electronic structure of the paramagnetic atom and be correlated with chemical data.

This differentiation between oxidation states arises from the fact that different energy-level schemes are associated with ions containing different numbers of unpaired electrons. Thus, if it can be shown that the electron-resonance absorption results will only fit into a certain energy-level pattern and that this corresponds to a certain configuration, then the oxidation state of the atom is immediately confirmed. The factors of interest are therefore those from which the complex energy-level pattern of the ion can be deduced. Variation of the resonance line width with temperature is one such important factor. This arises from the fact that the Debye waves of the lattice can only share energy with the spin system *via* a coupling to the orbital motion of the electrons. If such coupling is strong, the compound will have to be cooled to very low temperatures before narrow absorption lines are obtained, and this implies that there are orbital levels quite close to the ground state for such strong spin–orbit interaction to be possible. Conversely, if it is found that the line width is independent of temperature, then the spin–orbit coupling must be very small and there must be a large splitting between the ground state and the next orbital level. It can be seen that a measurement of the variation of line width with temperature can therefore be used to distinguish between different energy-level patterns.

Another factor which will help to determine the energy-level pattern of the ion is the effective spin value of the ground state. This determines the number of electronic transitions which will be observed and can thus be very easily determined from measurements on a single crystal. Since one or more of the transitions may vary with orientation, more care has to be observed in interpreting the results obtained from a glass or powder, as those transitions will have been spread over a large field variation and may thus not be observed. Additional information can also be obtained from the *g*-values of the electronic transitions which measure the rate of divergence of the electronic levels with magnetic field. Similarly, the hyperfine interaction with the nuclear moments of the atom can also be used since both of these depend on the orbital-level splitting to some extent.

It is therefore possible by correlating all the observed facts to draw up a tentative energy-level pattern for the ion, and this is usually precise enough to distinguish one configuration from any possible alternative.

Results.—Table 1 lists the oxy-anions studied together with the paramagnetic results obtained. The ions are classified according to the number of unpaired electrons. Before considering the individual results in detail, we describe the energy level patterns for each configuration, together with the particular effects that each has on the observed electron-resonance absorption associated with the ground state.

For a tetrahedral XO_4 complex, Wolfsberg and Helmholz [1] have calculated the energies of molecular orbitals formed from linear combinations of *d*, *s*, and *p* atomic orbitals on the X atom and *p* orbitals on the oxygen ligands. Their results for MnO_4^- and CrO_4^{2-} are qualitatively very similar and suggest that the same level scheme would be applicable to other oxy-anions of the transition metals, particularly since McGlynn and Kasha [5] have recently come to similar conclusions concerning the interpretation of the visible and ultra-violet absorption spectra of many oxy-ions including MnO_4^- and CrO_4^{2-}. On the scheme proposed by Wolfsberg and Helmholz the 24 " valence electrons " of a complex like MnO_4^- completely fill a number of levels to produce a " closed-shell " structure. The next

[5] McGlynn and Kasha, *J. Chem. Phys.*, 1956, **24**, 481.

lowest-lying unfilled level, which these authors refer to as $(3t_2)$, consists of three degenerate molecular orbitals transforming under the representation T_2 of the tetrahedral group T_d. These are formed from d_{xy}, d_{yz}, d_{zx} orbitals on the central atom in antibonding combinations with π-type orbitals on the ligands, and Wolfsberg and Helmholz are able to interpret the visible and ultraviolet absorption spectra of MnO_4^- and CrO_4^{2-} in terms of excitation of electrons into this $3t_2$ level.

TABLE 1. *g-Values of the transition-metal oxy-anions.*

No. of unpaired electrons	1			2	
	$g_\perp$	$g_\parallel$		g	cm.$^{-1}$
MnO_4^{3-}	1·97	1·95	MnO_4^{3-}	2·0	0·01
CrO_4^{3-}	1·97	1·98	RuO_4^{3-}	2·0	0·02
ReO_4^{3-}	1·95	2·00	ReO_4^{3-}	2·08	0·12
			FeO_4^{2-}	$g = 2·14$—$2·00$	

One may conclude from these results that further electrons fed into a complex of this type will be accommodated in the $3t_2$ level which is altogether capable of holding six electrons. Thus transition-metal complexes similar to MnO_4^{2-} would have the electronic configuration (closed-shells) $(3t_2)^1$, whilst those similar to MnO_4^{3-} would have two electrons in the $3t_2$ level.

If it is assumed that the state of least energy obtained from the configuration $(3t_2)^n$ is the one which has the maximum spin compatible with the Pauli principle,[6] then the ground states arising from the configurations mentioned above are as follows:

(*a*) $(3t_2)^1$. The ground state consists of three orbital states (transforming under the representation T_2 of T_d), each of which has a double spin degeneracy. The orbital degeneracy will be lifted by pertubations arising from distortions of the tetrahedron and from external crystalline fields, but the splitting will be comparatively small. Thus it would be expected that the lowest state of a complex of this type will be doubly degenerate (spin degeneracy) and will lie fairly close to the first excited states.

Application of an external magnetic field will remove the spin degeneracy, and a single electronic transition between the two states of the ground doublet is possible. Because of the other low-lying levels the line width of the absorption should vary markedly with temperature.

(*b*) $(3t_2)^2$. The ground state consists of three orbital states (transforming under the representation T_1 of T_d), each of which has a triple spin degeneracy arising from the presence of two unpaired electrons ($S = 1$). Pertubations due to distortions of the tetrahedron, etc., will remove the orbital degeneracy, and the spin degeneracy may also be partly lifted even in the absence of an external field. An external field will remove any remaining degeneracy in the ground state, and two electronic transitions will be possible. If there is a zero field splitting, these two transitions may be shifted relative to each other so that they do not overlap and two separate absorption lines will be obtained. Because of the other low-lying levels the width of these lines will be dependent on temperature.

An argument based on crystal-field theory leads to rather different conclusions. In this approach, the unpaired electrons are considered as being located entirely in *d* orbitals on the central metal atom, the ion being pictured as built up from a central positive ion and four oxide ligands (O^{2-}). The effect of the electric field produced by these four ligands in a tetrahedral arrangement round the central metal atom is to split the five *d* levels of the central atom into a group of two ($d\gamma$) levels lying below the remaining three ($d\varepsilon$) levels. If this splitting is applied as a perturbation to the lowest term arising from the ground configuration of the free ion, the results shown in Table 2 for differing numbers of unpaired *d* electrons are obtained. The table also shows results for an ion with six ligands arranged in an octahedron.[7] From the table it is evident that one can only expect narrow absorption lines at all temperatures from d^2 and d^5 tetrahedral complexes and d^3 and d^5 octahedral complexes.

[6] Stevens, *Proc. Roy. Soc.*, 1953, *A*, **219**, 542.
[7] van Santen and van Wieringen, *Rec. Trav. chim.*, 1952, **71**, 420.

The detailed results obtained from the different oxy-anions can now be considered and compared with the above conclusions.

(*a*) MnO_4^{3-}, ReO_4^{3-}, *and* CrO_4^{3-}. The paramagnetic resonance absorption spectra from all three of these complexes were found to consist of a single line which could only be observed at $T = 20°$ K. The rapid increase of line width with temperature, together with the effective spin value of $\frac{1}{2}$, is in agreement with the deductions made above and confirms that each of the compounds studied did in fact contain one unpaired electron.

TABLE 2.

Configuration	Spin degeneracy	Orbital degeneracy: tetrahedron	Orbital degeneracy: octahedron
d^1	doublet	doublet	triplet
d^2	triplet	singlet	triplet
d^3	quartet	triplet	singlet
d^4	quintet	triplet	doublet
d^5	sextet	singlet	singlet

The line shape was asymmetrical in each case, with a prominent shoulder on the side of the peak. This may be interpreted as a *g*-value variation, and the extreme values are listed in Table 1, the $_\perp$ suffix being associated with the peak, and the $_\parallel$ suffix with the shoulder. In the case of the manganate ion it has been found possible to make measurements on diluted single crystals and very much more information is thus available. The hyperfine structure from the $I = 5/2$ of the ^{55}Mn isotope can be clearly resolved and is found to be very anisotropic with extreme splittings of 150×10^{-4} cm.$^{-1}$ and 25×10^{-4} cm.$^{-1}$. A detailed analysis of these results will be published later.

(*b*) MnO_4^{3-}, ReO_4^{3-}, *and* RuO_4^{2-}. The most distinctive and readily interpretable electron-resonance spectrum in this group is obtained from the ruthenate ion. Two distinct electronic transitions are obtained, each with a slight spread but centred on apparent *g* values of 2·05 and 2·00 at 1·25 cm. wavelength. The separation is probably due to zero-field splitting of the spin triplet, and the two transitions have probably the same *g* value and a nearly isotropic splitting of 0·02 cm.$^{-1}$. This is in agreement with the postulated $(3t_2)^2$ configuration of the ruthenate ion. The absorption obtained from the hyporhenate ion is spread continuously over a relatively large field, its extremes corresponding to apparent *g* values of 2·50 and 2·08. This continuous range of absorption is probably to be attributed to the angular variation in splitting, however, and should thus be interpreted as arising from two electronic transitions with zero-field splitting varying from 0·00 cm.$^{-1}$ up to 0·12 cm.$^{-1}$. Only one broad line of 600 gauss width is obtained from sodium hypomanganate ($Na_3MnO_4.10H_2O$), but on dilution of the sample this absorption completely disappears. It would seem that this must be attributed to the sensitivity of the spin-triplet splitting to any irregular field symmetries which may arise in the diluted sample. These might well produce zero-field splitting so large that electron resonance is not possible with the frequencies available. Even this negative result is of use, however, since it is only configurations with an even number of unpaired electrons that can have all their degeneracy so removed by the action of internal electric fields. Each of the absorption lines obtained from the three ions was found to be temperature dependent. The MnO_4^{3-} ion had to be cooled to $T = 90°$ K before the signal was seen, whilst the lines obtained from RuO_4^{3-} and ReO_4^{3-} were only seen at $T = 20°$ K. This temperature dependence is what one would expect from a $(3t_2)^2$ configuration, but it is incompatible with the d^2 configuration of crystal field theory which would exhibit a line width independent of temperature.

The absorption signals obtained from the ferrate ion were of particular interest as there appeared to be a marked change of *g* value with temperature, from 2·14 at 20° K to 2·00 at 193° K. There also appears to be an appreciable difference between the absorption obtained from $BaFeO_4$ and K_2FeO_4. These results do not fit into the pattern outlined for covalent oxy-anions with two unpaired electrons and this problem is being studied in more detail.

Experimental

Electronic Technique.—It has been seen that one of the main features of interest in this work is the variation of the electron-resonance spectra with temperature. Low-temperature resonators have therefore been employed working at 1·25 cm. or 8 mm. wavelengths. These were of the standard type [8] employing nickel–silver wave-guide feed to a cylindrical cavity operating in the H_{111} mode, and were immersed in a tailed Dewar flask containing liquid oxygen, nitrogen, or hydrogen. The oxy-ion sample was placed centrally in the bottom of the cavity in the region of maximum microwave magnetic field, and normal crystal-video [9] methods of detection and display were employed. In this way the absorption lines can be observed directly on an oscilloscope screen, and the shape and width measured and photographed.

Preparation of Samples.—All reagents used were of " AnalaR " grade.

Solid potassium manganate was prepared and purified as described in Part I.[10] Potassium manganate–potassium sulphate mixed crystals were obtained from aqueous solutions of potassium hydroxide (4M), saturated with potassium sulphate at room temperature and containing potassium manganate at a concentration of about 10^{-2}M. This solution was concentrated rapidly by evaporation in an evacuated desiccator over potassium hydroxide pellets, and one of the very small crystals obtained on filtration was then used to seed the mother-liquor. This was concentrated slowly by bubbling through it a slow stream of purified dry nitrogen. By this simple method water vapour was slowly removed from the solution, carbon dioxide was excluded, and very gentle agitation of the solution was provided. Single crystals up to 4 mm. long were obtained.

Crystalline hydrated sodium hypomanganate was prepared as described in Part I.[10] Specimens of hypomanganate in an alkali glass were made by dissolving potassium permanganate in molten potassium hydroxide with access to air and cooling the hot blue solutions as rapidly as possible.

Dilute solutions of quinquevalent chromium were prepared in hot concentrated potassium hydroxide solution from potassium chromate. These solutions solidified to glasses at room temperature. No attempt has been made to isolate a crystalline derivative because of the extreme instability of the ion concerned. It is considered most probable that these green solutions contain the hypochromate CrO_4^{3-} ion. Details of the methods used for the preparation and the chemical procedures used to establish the valence state of this ion will be published separately.[11]

Solid potassium ferrate was prepared and purified by the method described by Hrostowski and Scott [12] and analysed as described by Schreyer.[13] The resulting solid was found to be at least 95% pure. Mixed microcrystals of potassium ferrate–potassium sulphate were obtained by saturation of an aqueous alkaline potassium ferrate solution with potassium sulphate and precipitation with solid potassium hydroxide. Barium ferrate was precipitated from a dilute alkaline solution of potassium ferrate by addition of barium chloride.

Sodium ruthenate was prepared in an alkali glass by dissolving finely divided ruthenium metal in molten sodium hydroxide and adding sodium peroxide.[14] The resulting solid dissolved in aqueous sodium hydroxide to give a clear orange solution which had an absorption spectrum identical with that described by Connick and Hurley [15] for the ruthenate ion.

Barium rhenate was obtained by fusion of barium per-rhenate (0·22 g.), rhenium dioxide (0·07 g.), and sodium hydroxide (1 g.) *in vacuo*.[16] The green mass was extracted with ethanol, leaving the insoluble barium rhenate as a dark green powder. By using a slight excess of per-rhenate it was ensured that no lower paramagnetic oxidation states of rhenium were present.

Potassium hyporhenate was prepared in an alkali glass by fusion of rhenium dioxide with the theoretical weight of potassium per-rhenate in molten potassium hydroxide *in vacuo*. No attempt was made to isolate the crystalline salt, since it is extremely unstable if free from alkali.

In order to ensure that the electron-resonance absorption lines studied were due to the

[8] Ingram, " Spectroscopy at Radio and Microwave Frequencies," Butterworths Scientific Publications, London, 1955, p. 66.
[9] *Op. cit.*, p. 94.
[10] Carrington and Symons, *J.*, 1956, 3373.
[11] Bailey and Symons, unpublished work.
[12] Hrostowski and Scott, *J. Chem. Phys.*, 1950, **18**, 106.
[13] Schreyer, *Analyt. Chem.*, 1950, **22**, 691, 1426.
[14] Krauss, *Z. anorg. Chem.*, 1924, **132**, 309.
[15] Connick and Hurley, *J. Amer. Chem. Soc.*, 1952, **74**, 5012.
[16] I. Noddack and W. Noddack, " Das Rhenium," Voss, Leipzig, 1933, p. 58.

oxy-anions as recorded, several checks were made. Thus in measuring the magnetic susceptibility of potassium ferrate, Hrostowski and Scott [12] found a marked field strength dependence and concluded that this was due to a ferromagnetic impurity, possibly ferric oxide or a ferrite. As a check on the behaviour of these possible impurities an aqueous solution of potassium ferrate was allowed to decompose to ferric oxide. In a second experiment potassium ferrate was allowed to decompose in very concentrated alkaline solution to give a solid solution of ferrite at room temperature. Neither of these samples showed any electron resonance either at room or at liquid-oxygen temperature.

In order to distinguish the signal obtained from the Cr^{V} ion from that caused by any Cr^{III} impurity, chromic chloride was dissolved in hot concentrated alkaline solution under oxygen-free conditions and cooled to a pale green glass. This gave a signal at room temperature, whereas the signal obtained from Cr^{V} was not seen above liquid-hydrogen temperatures.

In connection with the results obtained for the rhenate and hyporhenate ions, no resonance could be observed from rhenium dioxide.

One of us (A. C.) thanks the Esso Petroleum Company for the award of a Postgraduate Research Studentship.

THE UNIVERSITY, SOUTHAMPTON. [*Received, July 23rd,* 1956.]

---

922. *Picrotoxin and Tutin. Part VIII.**

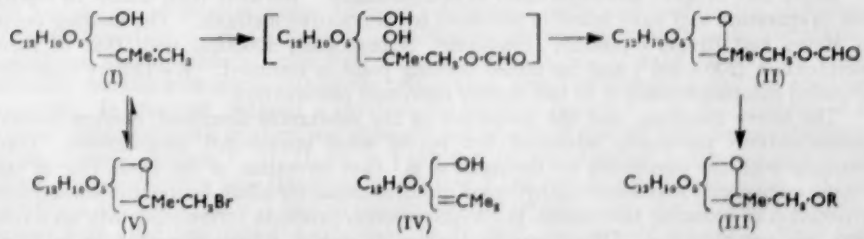
By R. B. JOHNS, S. N. SLATER, and R. J. WOODS (with, in part, D. BRASCH and ROY GEE).

Hydroxylation of the double bond of picrotoxinin has been studied and it is shown that with performic acid a product is obtained closely analogous to bromopicrotoxinin. Acylation and active-hydrogen studies are described. Reduction of picrotoxinin and several of its derivatives with lithium aluminium hydride is described, together with the action of periodic acid on the reduction products. The resulting evidence for a hemiacetal structure leads to tentative formulation of picrotoxinin as either (XX) or (XXI).

IN Part IV [1] the functional groups of the picrotoxin–tutin series of compounds were discussed. Further experiments bearing on this problem are now described.

THE DOUBLE BOND

Halogenation of picrotoxinin and tutin, giving saturated monohalogeno-compounds, is one of the most characteristic reactions in this series. It is closely paralleled by the hydroxylation of picrotoxinin (I) with performic acid to give hydroxypicrotoxinin formate (II), $C_{16}H_{16}O_8$, a saturated non-reducing compound hydrolysed by formic acid to

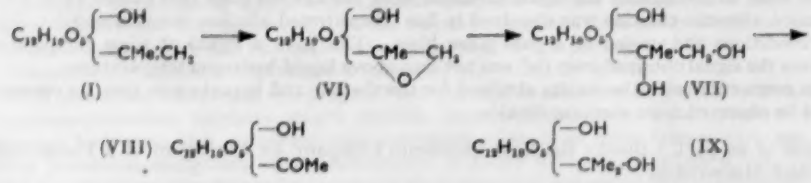


hydroxypicrotoxinin (III; R = H) which is stable to periodic acid and to lead tetra-acetate. Bromopicrotoxinin and hydroxypicrotoxinin are best formulated with the oxide ring on the tertiary rather than the primary carbon of the *iso*propyl group for the following reasons: (*a*) both picrotoxinin and *neo*picrotoxinin (IV) undergo bromination

* Part VII, *J.*, 1954, 1953.

[1] Benstead, Brewerton, Fletcher, Martin-Smith, Slater, and Wilson, *J.*, 1952, 1042.

in a similar fashion and it seems likely that the oxide ring is formed on the "unsaturated" carbon common to the two compounds; (*b*) hydroxypicrotoxinin readily forms a monoacetate (III; R = Ac) and gives a positive response to chromic acid in acetic acid, suggesting that it is a primary rather than a tertiary alcohol. The tertiary carbon atom of bromopicrotoxinin (V) is asymmetric and two isomerides are known. By contrast, hydroxypicrotoxinin formate was isolated in one form only, possibly because the entering group has a different steric requirement.



With perbenzoic acid, picrotoxinin gave an epoxide (VI), readily hydrolysed to dihydroxypicrotoxinin (VII) which is converted by periodic acid into α-picrotoxinone (VIII) and formaldehyde, which confirms the presence of a terminal methylene group. The stability of dihydroxypicrotoxinin is unexpected, since its formulation as (VII) suggests ready loss of water to give hydroxypicrotoxinin (III; R = H). This stability is presumably due to a sterically unfavourable configuration of the tertiary hydroxyl group. Although perbenzoic and performic acid give different products from picrotoxinin, no such difference is observed in the *neo*-series where, *e.g.*, acetyl*neo*picrotoxinin yields, with either reagent, acetylhydroxy*neo*picrotoxinin which according to its analysis and stability to periodic acid and to lead tetra-acetate lacks the α-glycol system. The oxide (VI) is a possible intermediate in conversion of picrotoxinin into picrotin (or an isomer) (IX) in which the presence of a dimethylcarbinol group seems established.

The presence in *neo*picrotoxinin (IV) of an *iso*propylidene group attached to a disubstituted carbon atom is confirmed by the ultraviolet absorption spectrum, which shows relatively strong absorption in the region 215—220 mμ (ε 3140 at 215 mμ) characteristic of tetrasubstituted double bonds.[2] No other derivative of picrotoxin showed strong absorption in this region.

Hydroxypicrotoxinin resembles bromopicrotoxinin in giving a hydroxy-acid (hydroxypicrotoxinic acid), $C_{15}H_{18}O_8$, with dilute aqueous sodium hydroxide. The same acid was obtained by treating α-picrotoxinic acid with perbenzoic acid, but performic acid yielded an isomeric acid. The relation between the two may be similar to that between α- and β-bromopicrotoxinic acid.

Meyer and Bruger [3] have described iodopicrotoxinin. We have been unable to repeat this preparation and have failed in attempts by alternative methods. The melting point of Meyer and Bruger's product (198—199°) is practically identical with that of their picrotoxinin (200—201°) and no mixed melting point is recorded. We believe that the so-called iodopicrotoxinin is in fact merely recovered picrotoxinin.

The above reactions, and the properties of the substances described, confirm certain generalisations previously advanced but reveal some unexpected irregularities. Consistently with the conclusion by Benstead *et al.*[4] that formation of the oxide ring of the bromo-compounds sequesters the hydroxyl group essential for alkali-fission and consequent generation of reducing substances, the hydroxylation products formulated with an oxide ring are non-reducing. Dihydroxypicrotoxinin resembles dihydropicrotoxinin in that, unlike picrotoxinin, it can be recovered from solution in cold dilute aqueous sodium hydroxide. Diazomethane has been postulated [4] as a reagent for distinguishing compounds of the "picrotin" series from those of the "picrotoxinin" series. This assumption is

[2] Bladon, Henbest, and Wood, *Chem. and Ind.*, 1951, 866; Halsall, *ibid.*, p. 867.
[3] Meyer and Bruger, *Ber.*, 1898, **31**, 2958.
[4] Benstead, Gee, Johns, Martin-Smith, and Slater, *J.*, 1952, 2292.

unjustified, since neither hydroxypicrotoxinin nor dihydroxypicrotoxinin is affected by diazomethane, and the behaviour of the picrotoxin series of compounds towards diazomethane remains therefore unpredictable and largely uncorrelated.

The Hydroxyl Groups (with D. Brasch and Roy Gee).—Because the functions of the non-lactonic oxygen atoms of picrotoxinin and picrotin are still incompletely defined we have made certain acylation and active-hydrogen studies. These help to define the number of hydroxyl groups present, although acylation can give only minimum numbers and active-hydrogen results give maximum numbers—particularly in complex lactonic molecules it is difficult to decide whether there are groups other than hydroxyl which can provide active hydrogen atoms.

There are numerous references to acylation but the results are confused partly because early workers started with picrotoxin, and partly owing to the absence of full analytical details.

Paterno and Oglialoro [5,6] heated picrotoxin with acetic anhydride and anhydrous sodium acetate to obtain a small amount of a substance, m. p. 227°, formulated as "picrotin acetic anhydride," $C_{19}H_{22}O_9$, and larger amounts of a substance, m. p. 245°, which reacted with bromine and was formulated as "picrotoxinin acetic anhydride," $C_{19}H_{22}O_8$. Meyer and Bruger [3] state that the acetylation of picrotoxinin itself with either acetic anhydride and sodium acetate or boiling acetyl chloride yields a picrotoxinin diacetate, $C_{19}H_{20}O_8$, m. p. 254—255°, believed identical with Paterno and Oglialoro's material of m. p. 245°. We have been unable to confirm the acetylation of picrotoxinin with boiling acetyl chloride, the starting material being recovered after about 30 minutes' reaction. No better success was achieved with cold acetic anhydride and perchloric acid, or with acetyl chloride and magnesium (Spassow's method [7]). Sielisch [8] described the acetylation of bromopicrotoxinin with acetyl chloride or acetic anhydride to a monoacetate, m. p. 268°. We have been unable to confirm either of these acetylations, and also failed with anhydride–perchloric acid and Spassow's method, bromopicrotoxinin being recovered unchanged. As already described, hydroxypicrotoxinin yields a monoacetate (III; R = Ac).

Paterno and Oglialoro [9] state that picrotin and boiling acetyl chloride give a mixture of picrotoxide and a substance, m. p. 202°, formulated initially as a diacetate, $C_{19}H_{22}O_9$, but later [5] as a monoacetate, $C_{17}H_{20}O_8$. Meyer and Bruger,[3] by treating picrotin first with cold and then with boiling acetyl chloride, obtained a mixture of anhydrodiacetylpicrotin, m. p. 300°, and a substance, m. p. 207—210° believed identical with Paterno and Oglialoro's material of m. p. 202°, but for which a diacetate formula was preferred; no acetyl determination was reported. Meyer and Bruger also studied the reaction between picrotin and acetic anhydride–anhydrous sodium acetate, isolating a substance, m. p. 244—245°, believed identical with the substance, m. p. 227°, obtained by Paterno and Oglialoro from picrotoxin (see above). On the basis of elementary analysis and acetyl figures, however, it was formulated as a monoacetate, $C_{17}H_{20}O_8$. We have examined the acetylation of picrotin under different conditions. First, we confirm the formation of the monoacetate, $C_{17}H_{20}O_8$, m. p. 242—243°, when picrotin reacts with acetic anhydride–anhydrous sodium acetate; also that of a diacetate, $C_{19}H_{22}O_9$, m. p. 200°. We have, however, worked with acetic anhydride rather than acetyl chloride and find the reaction complex. In the cold, without a catalyst, no reaction occurred. In the presence of a trace of sulphuric acid a mixture was obtained and separated into (*a*) acetyl*neo*picrotoxinin, (*b*) an isomeric acetate, $C_{17}H_{18}O_7$, m. p. 245°, and (*c*) high-melting material regarded as either anhydropicrotin (see above) or its acetate [3] but not further investigated. When anhydrous ferric chloride was used as catalyst several products were also isolated: at room temperature after five days the diacetate, m. p. 200°, was readily obtained; when the reaction mixture was heated the main product was anhydropicrotin; a systematic fractionation of the product obtained after the reaction mixture had been kept for two days yielded

[5] Paterno and Oglialoro, *Gazzetta*, 1879, **9**, 57.
[6] *Idem*, *ibid.*, 1881, **11**, 36.
[7] Spassow, *Ber.*, 1937, **70**, 1925.
[8] Sielisch, *Ber.*, 1912, **45**, 2555.
[9] Paterno and Oglialoro, *Gazzetta*, 1877, **7**, 193.

(i) a small amount of acetyl*neo*picrotoxinin, (ii) a somewhat greater amount of material regarded as the impure isomeric monoacetate, and (iii) mainly the diacetate.

Paterno and Oglialoro state that picrotin and benzoyl chloride give a monobenzoate, $C_{22}H_{22}O_8$, m. p. 230°, and Schmidt [10] describes a (mono)benzoylpicrotin, m. p. 245°. Meyer and Bruger [3] describe both a monobenzoylpicrotin, m. p. 236°, believed identical with Paterno and Oglialoro's material, and a dibenzoate, $C_{29}H_{26}O_9$, m. p. 247°, which was obtained at higher temperatures. The only benzoate we have succeeded in preparing is the monobenzoate, m. p. 236°.

From the above we conclude that picrotoxinin contains no acylatable group but that picrotin may form either a mono- or a di-acetate, and that under the influence of the acetylating agent used it may undergo dehydration to either *neo*picrotoxinin or an isomer not hitherto described but now isolated as its acetate. The existence of such an isomer had been earlier suspected.[11] The infrared spectrum of the acetate shows carbonyl absorption at 1732 and 1790 cm.$^{-1}$ and double-bond absorption at 1649 cm.$^{-1}$ (identical with that of picrotoxinin and tutin), suggesting that it differs from *neo*picrotoxinin in possessing an *iso*propenyl group. Its chemistry has not yet been investigated.

The acetylation of dihydroxypicrotoxinin (VII) is interesting. On the basis of the non-acetylation of picrotoxinin and the presence of only one additional (primary) hydroxyl group capable of ready acetylation, it would be expected to form a monoacetate. In fact, it forms a triacetate and thus behaves in a manner analogous to that of dihydropicrotoxinin, which (unexpectedly) gives a diacetate.[1]

Attempts have been made, particularly by Horrmann,[12] to determine the number of hydroxyl groups by the Zerewitinoff method. The numbers do not lie very close to whole numbers and Mercer and Robertson [13] attribute a value such as 1·5 for picrotoxinin to tenaciously held water of crystallisation. As we have never experienced difficulty in drying specimens for analysis it seemed to us more likely that the figure 1·5 was low rather than high, and due to incomplete reaction between picrotoxinin and the Grignard reagent under the conditions commonly used at that time (room temperature). Modern analytical practice requires heating of the reaction mixture.[14] We have therefore redetermined the active hydrogen content of picrotoxinin and related substances, using an apparatus essentially similar to that of Hochstein.[15] Table 1 shows the results, and also Horrmann's figures, from which it is reasonable to assume that Horrmann did, in fact, work at room

TABLE 1.

Substance	Active hydrogen by Grignard reaction			Active hydrogen by lithium aluminium hydride	
	Horrmann	at 30°	at 98°	at 30°	at 98°
Picrotoxinin	1·5	1·45, 1·48	2·12, 2·08	1·8	2·2
β-Bromopicrotoxinin	0·3	0·32, 0·32	0·93, 0·96	0·8	1·1
Reduced β-bromopicrotoxinin	—	—	4·90, 4·72	—	—
β-Bromopicrotoxinic acid	2·46	—	—	—	—
Methyl β-bromopicrotoxinate	—	1·80, 1·85	2·07, 2·10	1·8	2·1
Dihydropicrotoxinin	—	3·90, 3·90, 3·91	3·96, 3·95, 4·12	3·8	3·8
Dihydropicrotoxinin diacetate	—	—	4·02, 4·04	4·1	4·4
*neo*Picrotoxinin	—	2·91, 3·22	2·91, 3·22	3·2	3·3
Picrotin	2·1, 2·0	2·02, 2·00, 2·10	2·02, 2·00, 2·12	2·05	2·2
Acetylpicrotin	—	0·10, 0·10	0·12, 0·20	0·35	0·42
Benzoylpicrotin	—	1·51, 1·50	2·11, 2·06	1·8	2·2

temperature and that our figures at 98° represent completion of the initial reaction. The effect is particularly noticeable, for example, with β-bromopicrotoxinin. Lithium aluminium hydride is a useful alternative reagent for determining active hydrogen [16] and the Table gives also the figures obtained therewith.

[10] Schmidt, *Annalen*, 1883, **222**, 313.
[11] Slater and Wilson, *Nature*, 1951, **167**, 324.
[12] Horrmann, *Annalen*, 1916, **411**, 273.
[13] Mercer and Robertson, *J.*, 1936, 288.
[14] Pregl–Roth, ed. Grant, "Quantitative Organic Micro Analysis," Churchill, London, 4th edn., 1945, p. 134.
[15] Hochstein, *J. Amer. Chem. Soc.*, 1948, **70**, 305.
[16] Roger Adams, "Organic Reactions," Wiley, New York, 1951, Vol. VI, p. 469.

It seems clear that picrotoxinin contains two active hydrogen atoms and that one of these takes part in the bromination. If active hydrogen is equated with hydroxyl groups this is in accordance with views previously expressed.[4] The value of four active hydrogen atoms for dihydropicrotoxinin is unexpected. Hydrogenation of a double bond could conceivably remove an activating group and thus lower the figure, but would not be expected to raise it. An important difference has been observed, also, in the infrared spectra of the two substances—picrotoxinin absorbs at only one position in the 3μ region (at 3455 cm.$^{-1}$, in Nujol) whereas dihydropicrotoxinin has two bands (3527 and 3447 cm.$^{-1}$, in Nujol). The last bands are absent from the spectrum of diacetyldihydropicrotoxinin, which points to this substance's being a normal *O*-acetate and to the presence of two hydroxyl groups in dihydropicrotoxinin, as previously inferred. The fact that the diacetate still possesses four active hydrogen atoms may be due to the known activating influence of acetate groups on the hydrogen attached to adjacent carbon atoms.[17]

Picrotin shows only two active hydrogen atoms. This was unexpected, in view of the generally assumed relation between picrotin and picrotoxinin, and was at first attributed to incomplete reaction. In the Grignard reaction, however, no significant increase was obtained when a large volume of solvent was used (to decrease precipitation effects) and the reaction time was doubled. Again, *neo*picrotoxinin, the dehydration product of picrotin, shows an increase in its content of active hydrogen atoms over the latter, and acetyl- and benzoyl-picrotin give puzzling figures.

There is a clear conflict of evidence on the function of the sixth oxygen atom of picrotoxinin, which may be present in an ether or a hydroxyl group. The evidence in favour of two hydroxyl groups in dihydropicrotoxinin is very strong, and this, coupled with the active-hydrogen figures for picrotoxinin and β-bromopicrotoxinin and the lithium aluminium hydrogen reduction product of the latter (see below), suggests that picrotoxinin is a dihydroxy-compound. Against this is the somewhat uncertain relation between picrotoxinin and dihydropicrotoxinin.

If the sixth oxygen atom is part of a hydroxyl group, there must be either a third carbocyclic ring or a second double bond in picrotoxinin. The spectral evidence is against a second double bond. On the other hand the reaction between α-picrotoxinone and methanolic diazomethane leads to a compound, $C_{16}H_{18}O_7N_2$, corresponding to methylation of a hydroxyl group and addition of a second molecule of diazomethane, such as would be expected in the conversion of an olefin into a pyrazoline. A preliminary study of this compound by Mr. Ghulam Hassan has shown, however, that the infrared spectrum lacks absorption in the region expected for a C=N link, and the very ready loss of elementary nitrogen, either at the melting point or with cold mineral acid, also makes a pyrazoline structure unlikely. It may well be an intermediate of the type observed in reactions between aldehydes and diazomethane.[18] It is concluded that a second double bond is absent. There is no available evidence which bears closely on the question of a third carbocyclic ring.

No positive evidence for the presence of an ether linkage in picrotoxinin has hitherto been available, but strong experimental support is given below for the presence of a hemiacetal ether linkage, and in view of this it must be concluded that the balance of evidence is against a dihydroxy-structure for picrotoxinin. No explanation can be given for the anomalous behaviour of dihydropicrotoxinin.

The Lactone Groups and Centres of Acidity.—The high oxygen content of picrotoxinin and of picrotin suggests that lithium aluminium hydride reduction of these substances (or suitable derivatives) may produce polyhydric alcohols susceptible to attack by glycol-splitting reagents. Neither type of reaction is likely to proceed with isomerisation (such as accompanies all previously recorded degradations) and this offers hope of controlled stepwise degradation.

Reduction of β-bromopicrotoxinin, $C_{15}H_{15}O_6Br$, with lithium aluminium hydride gives (mainly) a crystalline alcohol, $C_{15}H_{23}O_6Br$, in which the increment of total hydrogen

[17] Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, 3rd edn., 1949, p. 521.
[18] Eistert, in "Newer Methods of Preparative Organic Chemistry," Interscience Publ. Inc., New York, 1948, p. 513.

and in active hydrogen corresponds to the complete reduction of two lactone groups. The product was stable to boiling 2N-sulphuric acid, to boiling 0·5N-sodium hydroxide, and to boiling acidified silver nitrate solution. A smaller quantity of a second crystalline reduction product, $C_{15}H_{21}O_6Br$, was also isolated. Since the only isomerisation likely to occur during the reduction is one analogous to that effected in passing from bromopicrotoxinin to bromopicrotoxinic acid, and reduction of the latter (see below) gives entirely different products, we assume that no such isomerisation has occurred. Debromination of the major reduction product has given small quantities of two crystalline products.

Reduction of picrotoxinin itself, $C_{15}H_{16}O_6$, gives somewhat intractable syrups, but a small quantity of crystalline material has been isolated. It is formulated as $C_{15}H_{20}O_6$, suggesting that only one of the two lactone groups has been reduced, but there is virtually no characteristic infrared absorption in the carbonyl region, and the substance is unaffected by methanolic sodium methoxide which would be expected to open any residual lactone ring [there is an extremely faint band at 1792 cm.$^{-1}$ (in Nujol) which we attribute to slight contamination with incompletely reduced material, but no corresponding absorption with the dihydro-derivative or the methyl ether, described below]. The alternative interpretation is partial reduction of both lactone groups.[19] The compound is non-reducing but may be degraded with alkali. It yields a methyl ether, $C_{16}H_{22}O_6$, with both diazomethane and methyl sulphate, and is smoothly hydrogenated to a derivative, $C_{15}H_{22}O_6$.

Reduction of either β-bromopicrotoxinic acid or its methyl ester gives in high yield a crystalline product, probably $C_{15}H_{21}O_6Br$. Its infrared spectrum shows medium absorption at 1639 cm.$^{-1}$ (in Nujol), whose origin is not apparent. Attempted debromination of the reduction product gave no useful material.

The actions of periodic acid and of lead tetra-acetate on the above reduction products have been closely studied but some unexpected difficulties have been encountered. The reaction with reduced β-bromopicrotoxinic acid appears most straightforward: Table 2

TABLE 2. *Periodic acid oxidation of reduced β-bromopicrotoxinic acid.*

Time (hr.)	35 min.	2	6	24	46
Reagent reacted (atoms of O/mol.)	1·05	1·1	1·15	1·35	1·55
Acid formed (equiv./mol.)	0	0	0	0·1	0·2

shows these results. The crystalline product, $C_{14}H_{17}O_5Br$, obtained in 95% yield, is accompanied by some formaldehyde. It has also been obtained by the action of potassium permanganate. It has an ultraviolet maximum at 302—305 mμ, strong carbonyl absorption at 1768 cm.$^{-1}$, and gives a 2 : 4-dinitrophenylhydrazone. It is therefore formulated as a five-membered cyclic ketone.[20] The expected alcohol, $C_{14}H_{19}O_5Br$, obtained by reducing the ketone with lithium aluminium hydride, is not attacked by periodic acid.

If β-bromopicrotoxinic acid is formulated as (X), these changes may be represented as follows, in which the carbonyl group is regarded as present in the five-membered ring which appears in a number of degradation products of picrotoxin:

$$C_{15}H_{19}O_4Br\{>C(OH)\cdot CO_2\text{—} \xrightarrow{LiAlH_4} C_{15}H_{17}O_4Br\{>C(OH)\cdot CH_2\cdot OH \xrightarrow{HIO_4}$$
(X)

$$C_{15}H_{17}O_4Br\{>CO \xrightarrow{LiAlH_4} C_{15}H_{17}O_4Br\{>CH\cdot OH$$

The action of periodic acid on reduced β-bromopicrotoxinin, $C_{15}H_{23}O_6Br$, is complex and appears to take place in two stages. The first (rapid) reaction consumes one mol. of reagent and is followed by slower consumption of periodate accompanied by expulsion of free bromine. Table 3 summarises the quantitative aspects of the reaction. Bromine appears in the reaction mixture after about three hours.

If the oxidation is carried out with periodate in neutral or alkaline solution, or with lead tetra-acetate in glacial acetic acid, only one mol. of reagent is consumed (see Table 3)

[19] Arth, *J. Amer. Chem. Soc.*, 1953, **75**, 2413; Hinder and Stoll, *Helv. Chim. Acta*, 1954, **37**, 1866.
[20] Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 114.

but the further action of acidic oxidising agents (periodic acid, iodic acid, acidified hydrogen peroxide) leads again to the expulsion of free bromine. Unfortunately no crystalline products could be isolated from the intermediate stage of oxidation, although two crystalline bromine-free end products, $C_{15}H_{22}O_7$ (?) and $C_{15}H_{24}O_6$ (?), have been obtained. Neither formaldehyde nor any other simple aldehyde or ketone has been regularly detected amongst the oxidation products (formaldehyde was identified once only). An important feature of Table 3 is that consumption of one mol. of periodic acid produces, from the

TABLE 3. *Oxidation of reduced β-bromopicrotoxinin*, $C_{15}H_{23}O_6Br$.

No.	Reagent	Time	Minutes 5	10	15	25	30	35	Hours 1	1·5
1	Periodic acid (acid solution)	Reagent reacted (atoms of O/mol.)	—	—	—	—	—	1·05	1·05	—
		Acid formed (equiv./mol.)	—	—	—	—	—	—	1·15	—
2	,,	$[\alpha]_D$ (assuming constant mol. wt.)	—	−86°	−76°	—	—	—	—	−76°
3	Periodate (alkaline solution [a])	Reagent reacting (atoms of O/mol.)	—	—	—	—	0·9	—	0·95	—
			—	—	—	—	1·05 [b]	—	1·0 [b]	—
		Acid formed (equiv./mol.)	—	—	—	—	1·45 [b]	—	1·35 [b]	—
4	Lead tetra-acetate	Reagent reacted (mol./mol.)	1·0	—	1·0	0·95	—	—	0·95	—

No.	Hours 2	3	5	7	7·5	18	21	23	24	45	47	48	72	90	116
1	1·0	—	—	1·4	—	—	—	2·1	—	—	2·95	—	—	—	—
	0·95	—	—	0·86	—	—	—	0·75	—	—	0·8	—	—	—	—
2	—	−76°	—	—	−66°	−60°	—	—	−60°	—	—	−48°	−49°	−47°	−46°
3	—	—	—	—	—	—	—	—	0·95	—	0·95	(2·0 [c])	—	—	—
	—	—	1·0 [b]	—	—	—	1·05 [b]	—	—	1·05 [b]	—	—	—	—	—
	—	—	1·05 [b]	—	—	—	0·9 [b]	—	—	0·9 [b]	—	—	—	—	—
4	0·95	—	—	—	—	—	—	—	1·1	—	—	1·2	—	—	—

[a] The oxidising medium was just alkaline to phenolphthalein. [b] A series of determinations in which the periodate reacting and the acid formed were determined simultaneously. [c] A portion of the solution was removed and acidified after 24 hr. and the periodate reacting determined after a further 23 hr.

completely neutral starting material, one equivalent of (back-titratable, *i.e.*, lactonic) acidity. This requires, in reduced bromopicrotoxinin, the grouping $-C(OH)\cdot C(OH)\cdot O-$ (with the second C also bonded to C) which on periodate cleavage would generate lactone and carbonyl functions. It is significant that the formula $C_{15}H_{22}O_7$ may be derived from $C_{15}H_{23}O_6Br$ by the two formal operations, (*a*) periodate cleavage, *i.e.*, loss of 2H, and (*b*) replacement of bromine by hydroxyl. Conductometric titration of the compound $C_{15}H_{22}O_7$ confirms the presence of one centre of acidity and the infrared spectrum shows very strong γ-lactone-carbonyl absorption at 1759 cm.$^{-1}$ (in Nujol). There is no other carbonyl absorption and any ketonic function (the compound is non-reducing) must be present in, *e.g.*, hemiacetal form. The above considerations suggest the partial formulations of bromopicrotoxinin (and by inference picrotoxinin) as (XI), reduced bromopicrotoxinin as (XII), and the compound $C_{15}H_{22}O_7$ as (XIII, modified by subsequent hemiacetal formation). The postulated hemiacetal-lactone system (XI) has implications on the lactonic behaviour and spectra of picrotoxinin and bromopicrotoxinin, which are discussed below.

The second periodate oxidation product, $C_{15}H_{24}O_6$, appears from its infrared spectrum [medium absorption at 1712 cm.$^{-1}$ (in Nujol)] coupled with its non-reducing properties, to be a ketone although no carbonyl derivatives have been obtained.

Experiments designed to avoid elimination of halogen during periodate oxidation

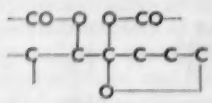
and to obtain more conclusive evidence on the fate of the carbonyl function generated are being actively pursued.

Table 4 summarises the action of periodic acid on the second reduction product of β-bromopicrotoxinin, $C_{15}H_{21}O_6Br$.

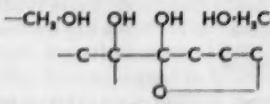
TABLE 4. *Periodic acid oxidation of reduced* β*-bromopicrotoxinin*, $C_{15}H_{21}O_6Br$.

Time	30 min.	2 hr.	24 hr.	45 hr.
Reagent reacted (atoms of O/mol.)	0·65	0·65	0·95	1·15
Acid formed (equiv./mol.)	0·5	0·5	0·8	—

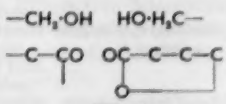
In previous papers of this series, especially Part IV,[1] attention has been drawn to the weakness of the evidence that the two titratable centres of acidity in picrotoxinin are the two lactone groups present. There is now increasing evidence that one may be an acidic hydroxyl group. Thus, (*a*) both bromopicrotoxinin and hydroxypicrotoxinin are monobasic only, the loss in each case of a hydroxyl group in the change from picrotoxinin being accompanied by loss of one unit of acidity, (*b*) the change of α- to β-picrotoxinic acid



(XI)

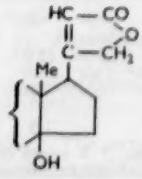


(XII)

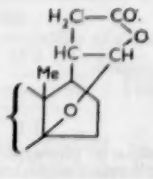


(XIII)

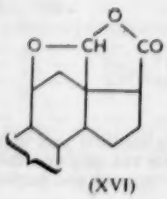
appears to sequester the hydroxyl group responsible for the "reducing" action of the former and this loss is accompanied by loss of one unit of acidity,[21] (*c*) reduced picrotoxinin, which lacks carbonyl absorption and cannot therefore be lactonic, still titrates as a monobasic substance, and (*d*) both picrotoxinin and reduced picrotoxinin yield methyl ethers



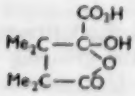
(XIV)



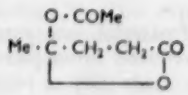
(XV)



(XVI)



(XVII)



(XVIII)

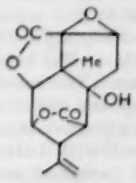
with diazomethane. If this view is correct it implies that one of the lactone groups of picrotoxinin and closely related compounds such as bromopicrotoxinin is stable to dilute aqueous alkali. This is readily intelligible if one of the lactones is of the hemiacetal type postulated above. Such a system is found in certain products derived from the cardiac glycosides; digitoxigenin and strophanthidin (XIV) give the "*iso*"-isomers (XV) under alkaline conditions, and the methods by which these compounds are prepared suggest that they are insoluble in dilute aqueous alkali, *i.e.*, that the hemiacetal-lactone group is stable under these conditions.[22] The grouping (XVI) also occurs in certain degradation products of the aldosteroids, and these likewise are not alkali-soluble.[23,24] Woodward and Eastman[25]

[21] Horrmann, *Ber.*, 1913, **46**, 2793.
[22] Ref. 17, p. 519.
[23] Simpson, Tait, Wettstein, Neher, von Euw, Schindler, and Reichstein, *Experientia*, 1954, **10**, 132.
[24] *Idem*, *Helv. Chim. Acta*, 1954, **37**, 1200.
[25] Woodward and Eastman, *J. Amer. Chem. Soc.*, 1950, **72**, 399.

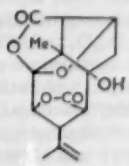
have drawn attention to the behaviour of the compound (XVII), which titrates as a monobasic acid.[26]

Picrotoxinin and related dilactonic compounds, examined in Nujol mull, all possess one lactone band in the infrared region at a higher wave number than that usually associated with saturated γ-lactones, *viz.*, 1780—1760 cm.$^{-1}$ (solution spectra):[27] thus for picrotoxinin, 1764; dihydropicrotoxinin, 1794; picrotoxinin epoxide, 1799; α-bromopicrotoxinin, 1784; β-bromopicrotoxinin, 1792; picrotin, 1803; *neo*picrotoxinin 1798; bromo*neo*picrotoxinin, 1797 cm.$^{-1}$. This frequency shift is observed in the simple hemiacetal-lactone γ-acetoxy-γ-valerolactone (XVIII), which absorbs[28] at 1797 cm.$^{-1}$; compounds in the series (XVI) absorb at the extreme of the normal range (1779 cm.$^{-1}$).

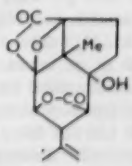
Further, if an ether link is present, the lithium aluminium hydride reductions show that it cannot be an ethylene oxide, as postulated by Conroy,[29] since this would suffer fission under such conditions. This view is supported by a comparison of the infrared spectra of picrotoxinin and its epoxide—that of the latter contains bands at 1234, 915, and 781 cm.$^{-1}$ attributable to the ethylene oxide ring but absent in the picrotoxinin spectrum (cf. Gunthard *et al.*[30]). It is also unlikely that any other simple ether linkage is present, since no such linkage is observed in any of the degradation products of known structure. On the other hand the hemiacetal link is not open to this criticism since it would be unlikely to survive vigorous degradation and it also provides a simple explanation of the very different effects of acid and alkali upon picrotoxinin.



(XIX)



(XX)



(XXI)

Although decisive degradative evidence is still lacking and the observed molecular rearrangements remain obscure, it is now possible to modify the Conroy formula (XIX) towards a more acceptable solution. This may be done (the sixth oxygen atom being assumed to be present in an ether linkage) by replacing the ethylene oxide ring by a hemiacetal-lactone system, as in (XX) or (XXI). Neither of these formulae is however completely satisfactory and additional work is required.

Experimental

Hydroxypicrotoxinin Formate (II).—17·1N-Hydrogen peroxide (2·0 ml.) was added to picrotoxinin (3·8 g.) in 98% formic acid (20 ml.), and the mixture allowed to evaporate at 35° overnight. The residue was crystallised from aqueous dioxan, to yield *hydroxypicrotoxinin formate* (2·28 g.). Recrystallisation gave the pure ester as needles, m. p. 237—238° (Found: C, 57·1; H, 4·7. $C_{16}H_{16}O_8$ requires C, 57·2; H, 4·8%). More crude ester (1·2 g.), m. p. 215—217°, was recovered from the mother-liquors.

Hydroxypicrotoxinin (III; R = H).—Hot 2·5% formic acid (20 ml.) was added to hydroxypicrotoxinin formate (0·5 g.) in hot dioxan (5 ml.), and the mixture refluxed for 1 hr. and then concentrated. The *hydroxypicrotoxinin* (0·35 g.), which gradually separated, was recrystallised from aqueous acetone, to give needles (grouped in plates resembling hoar frost), m. p. 249—250° (decomp.), $[\alpha]_D^{16}$ −90° (in acetone) (Found: C, 58·9; H, 5·65. $C_{14}H_{14}O_7$ requires C, 58·5; H, 5·25%). The *acetate* (III; R = Ac), prepared with acetic anhydride and anhydrous ferric chloride, crystallised from aqueous acetone in plates, m. p. 236° (Found: C, 58·1; H, 5·2; Ac, 13·5. $C_{17}H_{18}O_8$ requires C, 58·3; H, 5·2; Ac, 12·3%).

Dihydroxypicrotoxinin (VII).—(*a*) Perbenzoic acid (0·55 g., 1·05 mol.) in acetone (10 ml.) was

[26] Rothstein and Shoppee, *J.*, 1927, 531.
[27] Ref. 20, p. 153.
[28] Rasmussen and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1073.
[29] Conroy, *ibid.*, 1951, **73**, 1889.
[30] Gunthard, Heusser, and Furst, *Helv. Chim. Acta*, 1953, **36**, 1900.

added to picrotoxinin (1·1 g.) in acetone (40 ml.), and the solution kept at room temperature for 36 hr. and then allowed to evaporate. The solid residue, in chloroform, was diluted with ether, and the precipitate (0·75 g.) was crystallised several times from aqueous acetone, to give material, m. p. *ca.* 185° after much previous softening, which consisted largely of the epoxide (Found: C, 57·4; H, 5·8. Calc. for $C_{15}H_{16}O_7$: C, 58·5; H, 5·25%). It reacted with small quantities of lead tetra-acetate and of periodic acid. The mother-liquors from the crystallisation of the epoxide were concentrated to give a mixture of the epoxide and prisms of *dihydroxypicrotoxinin*. The former washed out with ether–acetone (1 : 1), and the latter, crystallised from aqueous acetone, had m. p. 262° (decomp.), $[\alpha]_D^{17}$ −65° (in acetone) (Found: C, 55·1; H, 5·45. $C_{15}H_{18}O_8$ requires C, 55·2; H, 5·55%). The compound consumed 1·01 mol. of periodic acid in aqueous methanol (1 : 1) during 1 hr. and 0·41 and 1·00 mol. of lead tetra-acetate in glacial acetic acid during 1 and 24 hr. respectively. The *triacetate*, prepared with acetic anhydride and anhydrous ferric chloride, crystallised from aqueous acetone as plates, m. p. 240° (Found: C, 56·1; H, 5·6; Ac, 28·1. $C_{21}H_{24}O_{11}$ requires C, 55·8; H, 5·35; 3Ac, 28·6%). (*b*) Perbenzoic acid (1·0 g.) in chloroform (16 ml.) was added to picrotoxinin (2·0 g.) in acetone (5 ml.), and the solution was allowed to evaporate overnight at 35°. The solid residue was dissolved in dioxan (10 ml.) and refluxed with 5% formic acid (40 ml.) for 1 hr. The resulting solution was washed with ether (3 × 20 ml.) and concentrated, to yield the dihydroxy-compound (1·6 g), identical with that described above.

α-Picrotoxinone (VIII).—Dihydroxypicrotoxinin (1·25 g.) was dissolved in hot water (20 ml.), cooled to about 50°, and treated with periodic acid (0·86 g., 1 mol.) in water (5 ml.). The mixture was kept at room temperature for 15 min. and then at 0° for 15 min. The crystals which separated (0·9 g.) were recrystallised from aqueous acetone to give α-picrotoxinone as needles, m. p. (variable according to conditions of heating) *ca.* 210—220°, $[\alpha]_D^{17}$ −10·3° (in EtOH) (Found: C, 56·8; H, 5·35. Calc. for $C_{14}H_{14}O_7$: C, 57·2; H, 4·8%). The ketone showed no depression of the m. p. when mixed with authentic α-picrotoxinone. The ketone was further characterised and identified by conversion into β-picrotoxinone (m. p. and mixed m. p. 252°) and picrotoxonic acid [m. p. and mixed m. p. 256° (decomp.)]. It gave a positive iodoform reaction.

The original filtrate from the α-picrotoxinone was neutralised with barium hydroxide, filtered, and distilled. Formaldehyde (0·71 mol.), estimated and identified as the dimedone derivative (m. p. and mixed m. p. 190°), was evolved.

Hydroxypicrotoxinic Acids.—(*a*) Sufficient dilute sodium hydroxide solution and water were added to hydroxypicrotoxinin (0·38 g.) in acetone (10 ml.) to give a homogeneous alkaline solution. The solution was set aside for 5 min., then made just acid (litmus) with hydrochloric acid and set aside for several days. The material which separated was taken up in the minimum quantity of dilute sodium hydroxide solution and acidified as above. The crystals which separated (0·30 g.) were recrystallised from water, to give the pure *acid*, m. p. 238—239° (decomp.), $[\alpha]_D^{18}$ −42° (in EtOH) (Found: C, 55·1; H, 5·9. $C_{15}H_{18}O_8$ requires C, 55·2; H, 5·55%). The acid did not react with lead tetra-acetate in acetic acid during 1 hr. (*b*) Sufficient dilute sodium hydroxide solution and water were added to hydroxypicrotoxinin formate (0·2 g.) in dioxan (5 ml.) to give a homogeneous alkaline solution. After 1 hr. the solution was made acid to Congo-red with hydrochloric acid, diluted with water (10 ml.), and concentrated to a thin syrup which deposited needles of hydroxypicrotoxinic acid (38 mg.) identical with the acid described above. (*c*) α-Picrotoxinic acid (0·7 g.) in acetone (5 ml.) was treated with perbenzoic acid (0·294 g.) in chloroform (7 ml.), and the mixture allowed to evaporate overnight. The crude solid was washed with ether and refluxed with dioxan (5 ml.) and 5% formic acid (20 ml.) for 2 hr. The solution was extracted several times with ether, concentrated, and kept for several days. The few crystals (*ca.* 20 mg.) which separated were identified by m. p. and mixed m. p. with the acid described above. (*d*) 17N-Hydrogen peroxide (0·4 ml.) was added to α-picrotoxinic acid (0·75 g.) in 95% formic acid (5 ml.), and the solution, after 5 hr. at 35°, was diluted with water (5 ml.) and left overnight. The solid formed (0·75 g.) crystallised from water, to give the isomeric *hydroxypicrotoxinic* acid as needles, m. p. 227° (decomp.), $[\alpha]_D^{18}$ −47·5° (in EtOH) (Found: C, 55·9; H, 6·2%). The acid did not react with lead tetra-acetate in acetic acid during 24 hr.

Acetylhydroxyneopicrotoxinin.—(*a*) Solutions of acetyl*neo*picrotoxinin (0·4 g.) in acetone (5 ml.) and of perbenzoic acid (0·18 g.) in chloroform (3·6 ml.) were mixed and kept at 25° for 5 hr. The solid residue, dissolved in acetone (5 ml.), was mixed with water (5 ml.) and 98% formic acid (1 ml.) and left at 25° for 10 hr. The residue was washed with ether (10 ml.), and the solid (0·346 g.) crystallised from aqueous acetone to give the *hydroxy-compound* as needles, m. p. 251—252° (Found: C, 58·8; H, 5·55; Ac, 11·9, 12·6. $C_{17}H_{18}O_9$ requires C, 58·3; H, 5·2;

Ac, 12·3%). It was recovered from treatment with periodic acid, formic acid, and sodium methoxide in methanol, and did not react with lead tetra-acetate in acetic acid during 1 hr. It readily reduced sensitised ammoniacal silver nitrate. (*b*) Acetyl*neo*picrotoxinin (0·25 g.), 17N-hydrogen peroxide (0·15 ml.), and 98% formic acid (3 ml.) were set aside overnight. The residue was repeatedly crystallised from aqueous acetone to give needles, m. p. 244°, showing no depression when mixed with the above hydroxy-compound (Found: C, 59·1; H, 5·55; Ac, 15·5%).

Reduction of Methyl β-Bromopicrotoxinate.—Methyl β-bromopicrotoxinate (21·8 g.) in dry dioxan (100 ml.) was added dropwise with stirring to a suspension of lithium aluminium hydride (11 g.) in dry ether (200 ml.), and the mixture refluxed for 30 min. Ethyl acetate (20 ml.) was added with cooling, followed by 2N-sulphuric acid (400 ml.). Solid sodium hydrogen carbonate was added until the mixture was just alkaline to litmus, and the whole was then evaporated to dryness under reduced pressure. The residue was refluxed with successive portions of absolute ethanol (5 × 200 ml.), and the combined extracts were evaporated under reduced pressure. The solid residue separated from water as crystals, m. p. 176° (12·5 g., 58%), raised by further crystallisation from water to 178°, $[\alpha]_D^{18}$ −90° (in EtOH) (Found, for hydrated material: C, 45·8; H, 5·75; Br, 20·4. $C_{15}H_{21}O_6Br,H_2O$ requires C, 45·6; H, 5·85; Br, 20·3. Found, for anhydrous material: C, 47·9, 47·8; H, 5·65, 5·7. $C_{15}H_{21}O_6Br$ requires C, 47·8; H, 5·6%). The *alcohol* did not reduce ammoniacal silver nitrate solution. It reacted with 0·48 and 0·98 mol. of lead tetra-acetate in acetic acid during 1 and 24 hr. respectively. Diazomethane is without effect on the compound, and conductometric titration failed to reveal any potential acidity. The same compound was obtained by reducing β-bromopicrotoxinic acid.

Reduction of β-Bromopicrotoxinin.—β-Bromopicrotoxinin (20 g.) was reduced with lithium aluminium hydride (11 g.) as described above. The crude solid (generally 5·2—6·2 g., m. p. *ca.* 210°) was crystallised from ethanol or water, to give the pure *alcohol*, m. p. 219° (decomp.), $[\alpha]_D^{19}$ −112° (in EtOH) (Found: C, 48·0, 47·95; H, 6·4, 6·25; Br, 21·0, 22·95. $C_{15}H_{23}O_6Br$ requires C, 47·5; H, 6·1; Br, 21·2%). The alcohol gave an amorphous *p-nitrobenzoate* (Found: C, 52·5, 52·6; H, 3·4, 3·9; N, 5·3. $C_{26}H_{29}O_{10}N_2Br$ requires C, 52·3; H, 3·9; N, 5·1%), absorption bands (3μ region) at 3485 and 3455 cm.$^{-1}$ (no CO absorption).

A portion of the mother-liquor from which the crude alcohol had separated was dissolved in dilute aqueous sodium hydroxide and continuously extracted with ether. The ether extract yielded a neutral syrup which deposited a little of the crystalline alcohol on long storage. The alkaline solution was then acidified and extracted with ether. The extract yielded a syrup which slowly deposited crystals, further crystallised from ethanol to yield a second *alcohol*, m. p. (for two specimens) 203°, 205° (decomp.) (Found: C, 47·45; H, 5·5. $C_{15}H_{21}O_6Br$ requires C, 47·75; H, 5·6%). The compound lacked absorption in the carbonyl region of the infrared spectrum. It reacted with 0·55 mol. of lead tetra-acetate in acetic acid during 1 or 24 hr.

Reduction of Picrotoxinin.—Picrotoxinin was reduced with lithium aluminium hydride as described above, and the crude syrup from several preparations chromatographed on alumina. One fraction, which reacted with 0·49 mol. of lead tetra-acetate in acetic acid during 1 hr., deposited a small quantity of a *compound* which formed large plates (from methanol), m. p. 212° (Found: C, 60·85, 61·1, 60·85, 60·65; H, 7·25, 7·25, 6·9, 6·9. $C_{15}H_{22}O_6$ requires C, 60·8; H, 6·8%).

Methylation of Reduced Picrotoxinin.—(*a*) Ethereal diazomethane was added to the alcohol (50 mg.), dissolved in methanol (10 ml.), to yield the *methyl ether* which crystallised from methanol in needles (16 mg.), m. p. 170° (Found: C, 62·4; H, 7·09. $C_{16}H_{22}O_6$ requires C, 61·9; H, 7·1%). (*b*) The alcohol (57 mg.) was dissolved in the minimum quantity of 40% aqueous potassium hydroxide, diluted with a little water, warmed slightly, and then treated with methyl sulphate (4 drops), the mixture remaining alkaline. The solution was warmed for a few minutes, acidified with sulphuric acid, and extracted five times with ethyl acetate. The extract was evaporated, to yield a solid which crystallised from ethanol (yield, 10 mg.) and then aqueous ethanol and had m. p. 176° [mixed m. p. with the product from (*a*), 171°].

Hydrogenation of Reduced Picrotoxinin.—The alcohol was hydrogenated in the presence of platinum to give the *derivative* (Found: C, 60·3; H, 7·68. $C_{15}H_{22}O_6$ requires C, 60·4; H, 7·4%).

Attempted Debromination of Reduced Bromopicrotoxinin.—The reduced bromopicrotoxinin was treated with zinc dust and ammonium chloride in the usual way, to give a syrup from which, by conventional methods, small quantities of a non-reducing substance, m. p. 226°, were obtained. By working up mother-liquors a second compound was obtained as needles (from methanol), m. p. 153° (Found: C, 59·9; H, 7·05. Calc. for $C_{15}H_{22}O_6$: C, 60·4; H, 7·4.

Calc. for $C_{15}H_{24}O_4$: C, 60·0; H, 8·05%), which did not react with lead tetra-acetate in acetic acid.

Reaction of Reduced β-Bromopicrotoxinic Acid with Periodic Acid.—A solution of periodic acid (7·0 g.) in water (35 ml.) was shaken with the reduction product (7·6 g.) in water (75 ml.) at 50°. The resulting semisolid mass, after 30 min. at 0°, was filtered off and washed with water. The *ketone* (7·25 g.) crystallised from water in needles, m. p. 200—201°, $[\alpha]_D^{18}$ −46·5° (in acetone) (Found: C, 48·85, 48·8; H, 5·45, 5·0; O, 22·9; Br, 22·8. $C_{14}H_{17}O_5Br$ requires C, 48·7; H, 4·9; O, 23·2; Br, 23·2%). It does not reduce ammoniacal silver nitrate, is unaffected by diazomethane, and gives a **2 : 4-*dinitrophenylhydrazone***, sparingly soluble in ethanol from which it crystallises in yellow needles, m. p. 282° (decomp.) (Found: C, 46·1; H, 4·0; N, 11·1. $C_{20}H_{21}O_8N_4Br$ requires C, 45·7; H, 4·0; N, 10·7%). The ultraviolet spectrum of the ketone shows a maximum at 302—305 mμ (ε 31).

The filtrate from the crude ketone was neutralised with barium hydroxide solution, filtered, and distilled. The distillate yielded the dimedone derivative of formaldehyde, m. p. and mixed m. p. 187° (0·09 mol.).

Reduction of the Ketone.—The ketone (0·75 g.) was reduced with lithium aluminium hydride to a product which crystallised in needles (0·46 g.) from water. Recrystallised, the *alcohol* had m. p. 174° and showed a marked depression when mixed with the reduction product, m. p. 178°, of β-bromopicrotoxinic acid itself (Found: C, 49·0; H, 5·9; Br, 21·3, 21·6. $C_{14}H_{19}O_5Br$ requires C, 48·4; H, 5·5; Br, 23·05%).

Reaction of Reduced β-Bromopicrotoxinin with Periodic Acid.—The alcohol $C_{15}H_{23}O_6Br$ (1·0 g.) was shaken with a solution of periodic acid (1·4 g.) in water (40 ml.) until dissolution was complete and then left overnight. During the reaction bromine was liberated. The solution was made just alkaline with barium hydroxide, filtered, acidified with a few drops of dilute sulphuric acid, filtered again, and then concentrated to half-volume under slightly reduced pressure. The concentrate was continuously extracted with ether to give, after removal of the ether, a glass (0·45 g.) which partially crystallised. The extraction was continued with ethyl acetate to give two fractions of which the first was solid (0·24 g.) and the second partly crystalline (0·26 g.). The solid products were combined and crystallised from water or ethanol, to give the *lactone*, m. p. 255° (decomp.), $[\alpha]_D^{18}$ −85° (in EtOH) (Found: C, 57·55, 57·05, 57·05; H, 6·85, 7·05, 6·85. $C_{15}H_{22}O_7$ requires C, 57·3; H, 7·05%). The lactone did not reduce ammoniacal silver nitrate or react with diazomethane.

A small quantity of a second product was obtained in one experiment as flat needles or rectangular plates (from ethanol), m. p. 227°, $[\alpha]_D^{20}$ −116° ± 13° (in EtOH) (Found: C, 60·45; H, 8·25. $C_{15}H_{24}O_4$ requires C, 60·0; H, 8·05%). It showed a mixed m. p. depression with the product, m. p. 226°, obtained in the debromination of reduced β-bromopicrotoxinin.

Acetylation of Picrotin.—(a) *With acetic anhydride and sulphuric acid.* Picrotin (2 g.), acetic anhydride (10 ml.), and concentrated sulphuric acid (2 drops) were set aside for 2 days and the resulting white precipitate (0·43 g.) was filtered off and recrystallised from much methanol; it then had m. p. >300°. The filtrate was decomposed with water, and the resulting precipitate (0·81 g.) was collected and fractionally crystallised from methanol to yield acetyl-*neo*picrotoxinin, m. p. and mixed m. p. 190° (Found: C, 60·7; H, 4·9; Ac, 12·6. Calc. for $C_{17}H_{18}O_7$: C, 61·1; H, 5·4; Ac, 12·9%), and a higher-melting, more soluble *isomer*, m. p. 245° sharp depression when mixed with monoacetylpicrotin of similar m. p. (Found: C, 60·6; H, 5·45; Ac, 12·3%). The latter compound was unsaturated towards alkaline permanganate.

(b) *With acetic anhydride and ferric chloride.* A small quantity of anhydrous ferric chloride was added to picrotin in excess of acetic anhydride. After 5 days the product was diluted with water, to yield the diacetate, which, crystallised from ethanol, had m. p. 200° (Found: C, 57·9; H, 5·6; Ac, 21·9. Calc. for $C_{19}H_{22}O_9$: C, 57·9; H, 5·6; 2Ac, 21·8%). If the reaction mixture is heated on the water-bath the main product is anhydropicrotin, m. p. and mixed m. p. 328° (Found: C, 62·0; H, 5·3. Calc. for $C_{15}H_{16}O_6$: C, 61·6; H, 5·5%).

Reaction between α-Picrotoxinone and Diazomethane (with Ghulam Hassan and G. R. Sleeman).—Ethereal diazomethane (slight excess) was added to α-picrotoxinone (0·4 g.) in methanol. After 2 hr. the solvent was removed under reduced pressure and the residue crystallised from methanol. The *ether* (0·39 g.) had m. p. *ca.* 202° (gas evolution; bath pre-heated to 190°) (Found: C, 54·8, 54·8; H, 5·2, 5·3; N, 8·1, 7·8; OMe, 9·6. $C_{16}H_{18}O_7N_2$ requires C, 54·85; H, 5·2; N, 8·0; OMe, 8·9%).

Reaction between β-Picrotoxinone and Diazomethane.—Under conditions similar to those described above a product was obtained, m. p. *ca.* 198° (gas evolution), mixed m. p. with the above substance, *ca.* 195° (Found: N, 8·1%).

We are greatly indebted to the Research Fund Committee of the University of New Zealand for research grants and for special Research Fellowships (to R. B. J. and R. J. W.). The microanalyses are mainly by the Microchemical Laboratory of the University of Otago, under the direction of Dr. A. D. Campbell, with supplementary analyses by the Micro-analytical Laboratory of the Division of Industrial Chemistry, C.S.I.R.O., Melbourne, under the direction of Dr. W. Zimmermann, and the Micro-analytical Laboratory of New York University, under the direction of Professor T. S. Ma. We are grateful to Professor L. H. Briggs, of Auckland University College, and the Director of the Dominion Laboratory, Wellington, for arranging infrared determinations and to Mr. I. R. C. McDonald for help in their interpretation.

VICTORIA UNIVERSITY COLLEGE,
AUCKLAND, NEW ZEALAND.

[*Received, May 5th,* 1956.]

---

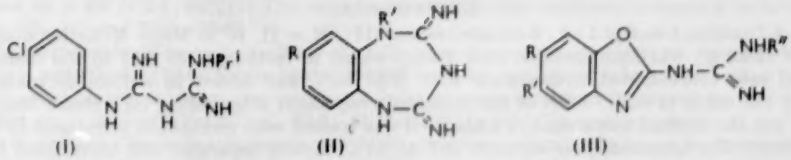
923. *Two Hypothetical Metabolites of Proguanil ("Paludrine").*

By R. M. ACHESON and N. F. TAYLOR.

Several benzoxazoles and benz-epines, modelled on proguanil, have been prepared from the appropriate amines and dicyandiamides or dicyanimide respectively. None of the compounds showed any antimalarial activity.

THE discovery [1] that proguanil ("Paludrine") (I) itself is not an antimalarial agent but that it is transformed *in vivo* into a highly active metabolite prompted speculation concerning the nature of the active material. The experiments here described were mostly carried out before the identification [2] of the metabolite as 4 : 6-diamino-1-*p*-chlorophenyl-1 : 2-dihydro-2 : 2-dimethyl-1 : 3 : 5-triazine.

Oxidative cyclisation of proguanil could give 5-chloro-2-N^3-*iso*propylguanidinobenziminazole, but this compound is inactive against *Plasmodium gallinaceum*.[3] An alternative cyclisation leads to the benzotriazepine (II; R = Cl, R′ = Pr^i). The unsubstituted derivative (II; R = R′ = H) had earlier [3] been obtained from *o*-phenylenediamine and dicyanimide. The 1-methyl derivative (II; R = H, R′ = Me) was formed under similar conditions from *N*-methyl-*o*-phenylenediamine and likewise did not react with aqueous nitrous acid. As the product from this reaction could have been 2-guanidino-1-methylbenziminazole, formed by reaction of one cyano-group of the dicyanimide with the diamine to give 2-cyanoamino-1-methylbenziminazole followed by addition of the ammonia produced to



the second cyano-group, this compound was prepared from *N*-methyl-*o*-phenylenediamine and dicyandiamide; its monopicrate was different from the dipicrate obtained from the triazabenzepine (II; R = H, R′ = Me) under the same conditions. The chlorobenzotriazepines (II; R = Cl, R′ = H, Et, and Pr^i) were then synthesised from the appropriate diamines, obtained by the catalytic reduction of the corresponding nitro-amines and isolated as the picrates which were then converted into the sulphates. The normal course of a *P. gallinaceum* infection in chicks was not, however, altered by the benzotriazepine (II; R = R′ = H) or any of its substituted derivatives described here; we thank Miss A. Bishop and Mrs. A. M. Yates for this information.

Hydroxylation of sulphanilamide *ortho* to the amino-group in man and rabbits,[4] and of

[1] Hawking, *Nature*, 1947, **159**, 409.
[2] Crowther and Levi, *Brit. J. Pharmacol.*, 1953, **8**, 93, and earlier papers.
[3] Acheson, King, and Spensley, *Nature*, 1947, **160**, 53; *J.*, 1948, 1366.
[4] Williams, *Biochem. J.*, 1946, **40**, 219; 1947, **41**, 1.

orthanilamide in rabbits,[5] has been established. A similar substitution of proguanil followed by elimination of ammonia would lead to the benzoxazole (III; R = Cl, R′ = H, R″ = Pr^i) which was next synthesised. The unsubstituted benzoxazole [6] and two derivatives [7] had been obtained earlier from the *o*-aminophenols, hydrochloric acid, and dicyandiamide. This condensation was used for the synthesis of the benzoxazoles (III; R = R″ = H, R′ = OMe; R = Cl, R′ = R″ = H; and R = R′ = Cl, R″ = H). The 2-*N*^{3}-*iso*propylguanidinobenzoxazoles (III; R″ = Pr^i) were obtained similarly but were much more difficult to crystallise. Early attempts to isolate the benzoxazole (III; R = Cl, R′ = H, R″ = Pr^i) from the reaction mixture as the picrate, which was purified, gave only 2-amino-6-chlorobenzoxazole picrate, but once the crude base (III) had been obtained crystalline direct from the reaction mixture no further difficulty was encountered. Imperial Chemical Industries Limited, Dyestuffs Division, in 1953 kindly tested the benzoxazoles (III; R = R″ = H, R′ = OMe) against *P. berghei* and *P. gallinaceum*, and the compound (III; R = Cl, R′ = R″ = H) against *P. gallinaceum*, but they proved inactive. We have been informed that this is also the case with the hypothetical metabolite (III; R = Cl, R′ = H, R″ = Pr^i) of proguanil.

In our hands Roberts and Rhys's synthesis [8] of 2-amino-5-chlorophenol proved more satisfactory than that of Theilacker's.[9] 5-Chloro-2-nitrophenol could be obtained only in very small yield from 2 : 4-dichloronitrobenzene and sodium hydroxide under a variety of conditions. *m*-Chlorophenol was obtained crystalline for the first time and in improved yield by modifying a published method.[10] There appears to be no rigorous proof in the literature of the structure of 1 : 2-dichloro-4 : 5-dinitrobenzene. The nitro-groups must be *ortho* to each other as condensation with ribitylamine, reduction, and then condensation with alloxan afford a dichloro-9-ribityl*iso*alloxazine. The *iso*alloxazine is isomorphous with vitamin B$_2$.[11] This suggests strongly that the structure given to the chlorodinitrobenzene is correct and it is supported by some infrared absorption measurements. Williams [12] and Thompson [13] have shown that in a series of 1 : 2 : 3 : 4-tetrasubstituted benzene derivatives a pronounced absorption band at 12·12 μ is consistent with vibrations of the vicinal hydrogen atoms on the benzene rings; for 1 : 2 : 4 : 5-tetrasubstituted derivatives absorption is usually minimal here but takes place in the 11·36—11·62 μ region. 1 : 2-Dichloro-4 : 5-dinitro-, 1 : 2-dichloro-4-hydroxy-5-nitro-, and 1-amino-4 : 5-dichloro-2-hydroxybenzene described have minimum absorption in paraffin paste at *ca.* 12·1 μ, with maxima towards shorter and longer wavelengths, while 1 : 2-dichloro-4-nitrobenzene, examined for comparison, had a very strong absorption maxima at 12·11 μ.

Experimental

2 : 4-*Diamino*-1-*methyl*-1 : 3 : 5-*benzotriazepine* (II; R = H, R′ = Me).—*N*-Methyl-*o*-nitroaniline (2·02 g.) was hydrogenated over Raney nickel in methanol (20 ml.) to the diamine, filtered into concentrated hydrochloric acid (1·32 ml.), and added to sodium dicyanimide (1·17 g.) in water (5 ml.). Most of the methanol evaporated after boiling on a steam-bath for 1 hr., and the residual suspension of a black oil was treated with methanolic picric acid (6·0 g., 2·0 mol.). The *benzotriazepine dipicrate* (5·9 g., 68%) rapidly separated and crystallised from methanol (charcoal) in yellow needles, m. p. 216—217° (decomp.) (Found: C, 39·1; H, 2·8; N, 23·1. $C_9H_{11}N_5,2C_6H_3O_7N_3$ requires C, 38·9; H, 2·6; N, 23·8%). Decomposition of the dipicrate in hot 2-ethoxyethanol solution with alcoholic sulphuric acid gave the *sulphate*, precipitated by ether. After being washed with ether (to remove picric acid) this separated from aqueous ethanol in colourless needles, m. p. 252° (decomp., after softening at ~230°) (Found: C, 33·8; H, 5·8; N, 22·2; S, 9·5. $C_9H_{11}N_5,H_2SO_4,2H_2O$ requires C, 33·4; H, 5·3; N, 21·7; S, 9·9%).

The sulphate (0·2 g.), suspended in sulphuric acid (0·053 ml.; *d* 1·84) in water (2 ml.), was

[5] Stubbs and Williams, *Biochem. J.*, 1947, **41**, xlix.
[6] Smith, Kane, and Mason, *J. Amer. Chem. Soc.*, 1929, **51**, 2522.
[7] Nagano, Itoh, and Matsumura, *J. Amer. Chem. Soc.*, 1953, **75**, 2770.
[8] Roberts and Rhys., *J.*, 1937, 41.
[9] Theilacker, *Ber.*, 1938, **71**, 2065.
[10] Fieser and Thompson, *J. Amer. Chem. Soc.*, 1939, **61**, 382.
[11] Kuhn, Weygand, and Moller, *Ber.*, 1943, **76**, 1044.
[12] Williams, *Rev. Sci. Instr.*, 1948, **19**, 135.
[13] Thompson, *J.*, 1948, 328.

treated with 10% aqueous sodium nitrite (0·86 ml.). No visible reaction took place in 2 hr. at room temperature and a sample gave no colour with alkaline β-naphthol. When heated to 90° the solid dissolved and after 1 hr. aqueous sodium picrate (0·32 g.) was added. The original benzepine dipicrate (0·28 g., 70%), m. p. and mixed m. p. 216—217° (decomp.), was precipitated.

2 : 4-*Diamino*-7-*chloro*-1 : 3 : 5-*benzotriazepine* (II; R = Cl, R′ = H).—The *benzotriazepine monopicrate* (4·05 g., 79%) was similarly prepared from 5-chloro-2-nitroaniline (2·02 g.), concentrated hydrochloric acid (1·17 ml.), sodium dicyanimide (1·04 g.), and picric acid (2·7 g.) and crystallised from methanol in short yellow needles, m. p. 263—264° (Found: C, 38·6; H, 2·5; Cl, 8·3. $C_8H_8N_8Cl,C_6H_3O_7N_3$ requires C, 38·3; H, 2·5; Cl, 8·1%). The *hemisulphate hemihydrate*, prepared from the picrate as above, separated from a large volume of water in colourless needles, m. p. 274° (decomp.) (Found: C, 36·0; H, 4·1; S, 6·0. $C_8H_8N_8Cl,\frac{1}{2}H_2SO_4,\frac{1}{2}H_2O$ requires C, 35·9; H, 3·7; S, 6·0%).

2 : 4-*Diamino*-8-*chloro*-1-*ethyl*-1 : 3 : 5-*benzotriazepine* (II; R = Cl, R′ = Et).—The *benzotriazepine dipicrate* (3·8 g., 58%) was similarly prepared from 5-chloro-*N*-ethyl-2-nitroaniline (1·90 g.), hydrochloric acid (0·95 ml.), sodium dicyanimide (0·85 g.), and picric acid (4·6 g.) and separated from aqueous methanol in irregular yellow prisms, m. p. 195—196° (decomp., with sintering at ~190°) (Found: C, 38·1; H, 2·9. $C_{10}H_{12}N_8Cl,2C_6H_3O_7N_3$ requires C, 37·8; H, 2·6%). The hydrated *sulphate*, obtained as before, separated from aqueous ethanol in colourless needles, m. p. 107—115° (with loss of solvent; after resolidification the colourless residue decomposed at ~170—180°) [Found: loss on drying at 100° *in vacuo*, 11·9; on dried material: S, 10·3. $C_{10}H_{13}N_8Cl,H_2SO_4,2\frac{1}{2}H_2O$ requires loss (to anhydrous material) 11·8; S (anhyd.) 9·5%].

2 : 4-*Diamino*-8-*chloro*-1-iso*propyl*-1 : 3 : 5-*benzotriazepine* (II; R = Cl, R′ = Pr^i).—The *benzotriazepine dipicrate* (17·2 g., 81%) was obtained as before from 5-chloro-2-nitro-*N*-*iso*propylaniline (6·4 g.), hydrochloric acid (3·0 ml.), sodium dicyanimide (2·66 g.), and picric acid (14·5 g.), and separated from ethanol as the solvate in thin yellow prisms, m. p. 208—210° (decomp. after sintering at ~180°) (Found: C, 39·7, 40·1; H, 3·4, 3·3; N, 20·0; Cl, 4·9. $C_{11}H_{14}N_8Cl,2C_6H_3O_7N_3,C_2H_5{\cdot}OH$ requires C, 39·7; H, 3·3; N, 20·4; Cl, 4·7%). Decomposition in 2-ethoxyethanol was unsatisfactory owing to the insolubility of the dipicrate, but its (11·7 g.) solution in hot *cyclo*hexanol (30 ml.) with concentrated sulphuric acid (6·0 ml.) in ethanol (20 ml.) followed by ether gave the *sulphate* (5·0 g., 86%) which was washed with ether and separated from aqueous ethanol in colourless plates, m. p. 175—177° (decomp.) (Found: C, 38·2; H, 4·6; S, 8·9. $C_{11}H_{14}N_8Cl,H_2SO_4$ requires C, 37·8; H, 4·6; S, 9·2%).

5-*Chloro*-N-*ethyl*-2-*nitroaniline*.—2 : 4-Dichloro-1-nitrobenzene (5·0 g.), ethylamine hydrochloride (4·3 g.), sodium hydroxide (2·1 g.), ethanol (10 ml.), and water (10 ml.) were slowly heated to 200° (5 hr.) in a sealed tube. The product was washed out with a little ethanol and diluted with water, and the amine collected. It separated from aqueous methanol in yellow prisms, m. p. 83° (4·2 g., 80%). This amine, prepared by other methods, is reported to have [14, 15] m. p. 83—84° and 75·5—76·5°.

5-*Chloro*-2-*nitro*-N-iso*propylaniline*.—2 : 4-Dichloro-1-nitrobenzene (8·4 g.), *iso*propylamine (5·2 g.), and ethanol (20 ml.) were heated at 200° for 6 hr. in a sealed tube. The *aniline* (8·3 g., 88%) was isolated as above, and separated from aqueous methanol (charcoal) in thin yellow needles, m. p. 50—51° (Found: C, 50·2; H, 5·5. $C_9H_{11}O_2N_2Cl$ requires C, 50·3; H, 5·1%).

2-*Guanidino*-1-*methylbenziminazole*.—*N*-Methyl-*o*-nitroaniline (4·0 g.) was hydrogenated to the diamine in ethanol (20 ml.) over Raney nickel and filtered into a mixture of concentrated hydrochloric acid (5·3 ml.), dicyandiamide (2·3 g.), and water (20 ml.). The mixture was refluxed (1 hr.) and methanolic picric acid (12·0 g., 2 mol.) added. The *benziminazole monopicrate* separated, and crystallised from ethanol (charcoal) in orange-yellow prisms, m. p. 193—195° (Found: C, 43·3; H, 3·3; N, 26·0. $C_9H_{11}N_5,C_6H_3O_7N_3$ requires C, 43·1; H, 3·3; N, 26·8%).

2-*Guanidino*-5-*methoxybenzoxazole* (III; R = R″ = H, R′ = OMe).—2-Amino-4-methoxyphenol (0·52 g.), ethanol (2 ml.), and hydrochloric acid (0·5 ml.; *d* 1·16) were heated to boiling, dicyandiamide (0·42 g.) added, and the whole heated under reflux for 2 hr. Water was added and the precipitate (0·7 g.) collected, dissolved in boiling water (30 ml.), and basified with aqueous sodium hydroxide. The *benzoxazole* was precipitated, and crystallisation from water gave colourless needles, m. p. 214° (0·4 g., 45%) (Found: C, 52·5; H, 4·9; N, 27·2. $C_9H_{10}O_2N_4$ requires C, 52·5; H, 5·0; N, 26·7%). The *picrate* separated from aqueous ethanol in the small yellow needles of the trihydrate, m. p. 220° (Found: C, 36·9; H, 4·2; N, 20·2. $C_9H_{10}O_2N_4,C_6H_3O_7N_3$ requires C, 36·8; H, 3·9; N, 20·1%).

[14] Laubenheimer, *Ber.*, 1878, **11**, 1156.
[15] Stoermer and Hoffmann, *Ber.*, 1898, **31**, 2533.

6-Chloro-2-guanidinobenzoxazole (III; R = Cl, R′ = R″ = H).—This was prepared similarly from 2-amino-5-chlorophenol (0·28 g.), ethanol (2 ml.), hydrochloric acid (0·2 ml.), and dicyandiamide (0·16 g.), and crystallisation from water (charcoal) gave small colourless needles of the *monohydrate*, m. p. 202° (Found: C, 42·3; H, 4·0; Cl, 15·4. $C_8H_7ON_4Cl,H_2O$ requires C, 42·1; H, 3·9; Cl, 15·5%). The base sublimed at 120° *in vacuo*, but lost most of its water when dried on a steam-bath (1 hr.) and then over phosphoric oxide (Found: C, 46·1; H, 3·6. $C_8H_7ON_4Cl$ requires C, 45·6; H, 3·3%). The *picrate* separated from water in small yellow needles, m. p. 265° (decomp.) (Found: N, 21·3. $C_8H_7ON_4Cl,C_6H_3O_7N_3$ requires N, 21·5%).

5 : 6-Dichloro-2-guanidinobenzoxazole (III; R = R′ = Cl, R″ = H).—This was similarly prepared from 2-amino-4 : 5-dichlorophenol (0·54 g.), water (5 ml.), hydrochloric acid (0·5 ml.), and dicyandiamide (0·42 g.). A precipitate was formed after 15 minutes' refluxing, which was then continued only for a further 30 min. The *benzoxazole*, isolated as before, separated from aqueous ethanol in colourless needles (0·3 g.), m. p. 250° (Found: C, 39·4; H, 2·5. $C_8H_6ON_4Cl_2$ requires C, 39·2; H, 2·5%).

2-N³-iso*Propylguanidinobenzoxazole* (III; R = R′ = H, R″ = Pr^i).—2-Aminophenol (0·5 g.), water (2 ml.), and hydrochloric acid (0·5 ml.) were heated to boiling and *iso*propyldicyandiamide (0·52 g.) added. After refluxing (2 hr.) the mixture was cooled and basified and the aqueous layer decanted. The residual gum was warmed with water (10 ml.) and hydrochloric acid (0·5 ml.) until it dissolved. The *benzoxazole hydrochloride* (0·3 g.) was precipitated on cooling and separated from water, containing a trace of hydrochloric acid, in small colourless needles, m. p. 100° (Found: C, 45·7; H, 6·6; Cl, 13·6. $C_{11}H_{15}ON_4Cl,2H_2O$ requires C, 45·4; H, 6·5; Cl, 13·3%). The free *base*, obtained with aqueous alkali, separated from aqueous ethanol in prisms, m. p. 171° (Found: C, 60·9; H, 6·4. $C_{11}H_{14}ON_4$ requires C, 60·5; H, 6·4%). The *picrate*, yellow needles from 50% aqueous ethanol, had m. p. 202° (Found: C, 45·7; H, 3·8; N, 21·8. $C_{17}H_{17}O_8N_7$ requires C, 45·8; H, 3·9; N, 22·0%).

*5-Methoxy-2-(*N³-iso*propylguanidino)benzoxazole* (III; R = H, R′ = OMe, R″ = Pr^i).—This was similarly prepared from 2-amino-4-methoxyphenol (0·52 g.), water (2 ml.), hydrochloric acid (0·5 ml.), and *iso*propyldicyandiamide (0·52 g.). The *hydrochloride* (0·4 g.) separated from water containing a trace of hydrochloric acid as colourless needles, m. p. 216° (Found: C, 50·9; H, 6·0; N, 19·2. $C_{12}H_{16}O_2N_4,HCl$ requires C, 50·6; H, 6·0; N, 19·6%). The *picrate* separated from aqueous ethanol in yellow needles, m. p. 204° (Found: C, 45·5; H, 3·9; N, 19·8. $C_{18}H_{19}O_9N_7$ requires C, 45·3; H, 3·9; N, 20·5%).

*6-Chloro-2-(*N³-iso*propylguanidino)benzoxazole* (III; R = Cl, R′ = H, R″ = Pr^i).—2-Amino-5-chlorophenol (10·0 g.), *iso*propyidicyandiamide (10·6 g.), water (50 ml.), and hydrochloric acid (7·3 ml.; *d* 1·16) were refluxed (40 min.) and diluted with water (180 ml.). The precipitated oil solidified on seeding and crystallisation from water (150 ml.)–ethanol (100 ml.), with charcoal, gave the crude *benzoxazole* (2·3 g., m. p. 178—179°). It separated from aqueous ethanol in colourless prisms, m. p. 184° (Found: C, 52·3, 52·4; H, 5·1, 5·3; Cl, 14·8. $C_{11}H_{13}ON_4Cl$ requires C, 52·3; H, 5·1; Cl, 14·1%). The *picrate* separated from ethanol in yellow plates, m. p. 255° (decomp.) (Found: C, 42·2; H, 3·3; N, 20·2. $C_{17}H_{16}O_8N_7Cl$ requires C, 42·4; H, 3·3; N, 20·4%). Successive evaporation of the filtrate from this benzoxazole at room temperature gave a series of precipitates, the m. p.'s of which descended to *ca.* 140° before rising again. The last fraction (0·53 g.), m. p. 170—174°, after five crystallisations from ethanol, gave 2-amino-6-chlorobenzoxazole, m. p. 182—183°, mixed m. p. 183—184°, and mixed m. p. with the oxazole (III; R = Cl, R′ = H, R″ = Pr^i) 144—150°.

In some early experiments when the reaction mixture was refluxed for 2 hr. the dark oil which separated did not crystallise. It gave a crystalline picrate with ethanolic picric acid, and crystallisation from ethanol gave small yellow needles, m. p. and mixed m. p. 219°, of *2-amino-6-chlorobenzoxazole picrate* (Found: C, 39·7; H, 2·3; N, 16·8. $C_{13}H_8O_9N_6Cl$ requires C, 39·2; H, 2·0; N, 17·6%). This picrate was dissolved in 2-ethoxyethanol and treated with *n*-propanolic hydrogen chloride followed by dry ether. The corresponding *hydrochloride* was precipitated, and was obtained as a colourless solid, m. p. 208°, by reprecipitation from propanol by ether (Found: C, 40·7; H, 3·1; N, 12·7. $C_7H_6ON_3Cl_3$ requires C, 40·9; H, 2·9; N, 13·6%). The free *base* separated from aqueous ethanol in colourless prisms, m. p. and mixed m. p. 184° (Found: C, 49·9; H, 2·9. $C_7H_5ON_3Cl$ requires C, 49·9; H, 3·0%).

2-Amino-6-chlorobenzoxazole.—2-Amino-5-chlorophenol (1·44 g.) in ethanol (5 ml.) was added to cyanogen bromide (1·06 g.); the mixture darkened and became warm. After 2 days at room temperature warm water was added to dissolve the crystalline precipitate, followed by aqueous sodium hydroxide. *2-Amino-6-chlorobenzoxazole* (1·40 g., 83%) was precipitated and separated from aqueous ethanol in pale yellow rhombs, m. p. 184° (Found: C, 50·0; H, 3·0; N, 15·8%),

depressed to ~145° on admixture with 6-chloro-2-(*N*^{3}-*iso*propylguanidino)benzoxazole. The *picrate*, yellow needles from aqueous ethanol, had m. p. 219° (Found: C, 39·1; H, 2·1%).

m-*Chlorophenol.*—*m*-Chloroaniline (161 g.) was diazotised according to Fieser and Thompson's method [15] and the solution added dropwise to a mixture of water (520 ml.), sulphuric acid (540 ml.; *d* 1·84), and copper sulphate pentahydrate (150 g.) that was being steam-distilled. The temperature of the diazotised solution was kept below 5° until immediately before the addition. Extraction of the distillate (5—6 l.) with ether, followed by distillation, gave the phenol (70—75% yield), b. p. 210—214°, deliquescent yellow needles, m. p. 31—32°.

1 : 2-*Dichloro*-4 : 5-*dinitrobenzene.*—This was prepared according to Turner and Le Fèvre's method [16] and the crude product crystallised twice from glacial acetic acid–water (4·5 : 1 by volume). The product separated in colourless plates, m. p. 110°, and showed the following absorption maxima in the 11—13 μ region: 11·10, 11·34, 11·73, and 12·77 μ.

4 : 5-*Dichloro*-2-*nitrophenol.*—1 : 2-Dichloro-4 : 5-dinitrobenzene (1·2 g.) was refluxed with sodium hydroxide (0·4 g.) in water for 5 hr. Acidification of the deep red solution precipitated the *nitrophenol* (1·0 g.) which crystallised from aqueous ethanol as yellow prisms, m. p. 68° (Found: C, 34·9; H, 1·6; N, 6·8; Cl, 33·9. $C_6H_3O_3NCl_2$ requires C, 34·6; H, 1·4; N, 6·7; Cl, 34·0%). Its infrared absorption spectra showed maxima at 11·20, 11·41, 11·64, 11·85, and 13·17 μ. Woolley and Pringle [17] report m. p. 70—71° but give no preparative details.

2-*Amino*-4 : 5-*dichlorophenol.*—Sodium dithionite (16 g.) in water (50 ml.) was added gradually with shaking to 4 : 5-dichloro-2-nitrophenol (4·2 g.) in hot water (20 ml.) and ethanol (50 ml.). The ethanol was distilled off and, on cooling, the aminophenol (3·0 g., 84%) was precipitated. Crystallisation from water gave colourless needles, m. p. 171—172° (Found: C, 40·5; H, 3·0; N, 7·7; Cl, 39·4. Calc. for $C_6H_5ON_2Cl_2$: C, 40·4; H, 2·8; N, 7·9; Cl, 39·9%). Its infrared absorption spectra showed maxima at 11·13, 11·55, 11·64, and 12·52 μ. Woolley and Pringle [17] give m. p. 174—175° and used the less convenient reduction by tin and hydrochloric acid.

3 : 4-*Dichloronitrobenzene.*—This was prepared from *o*-dichlorobenzene [18] and had m. p. 42°. It showed infrared absorption maxima at 11·31, 12·11, 12·56, and 12·97 μ.

We thank Dr. F. E. King, F.R.S., for his interest in the part of this work which was carried out in the Dyson Perrins Laboratory, and Mr. A. O. Plunkett for some technical assistance.

Dyson Perrins Laboratory, and
Laboratory of Human Nutrition, Department of Biochemistry,
South Parks Road, Oxford. [*Received, June 11th*, 1956.]

[16] Turner and Le Fèvre, *J.*, 1927, 1119.
[17] Woolley and Pringle, *J. Biol. Chem.*, 1952, **194**, 729.
[18] McMaster and Magill, *J. Amer. Chem. Soc.*, 1928, **50**, 3038.

---

924. *Several Quinoxalines of Biological Interest.*

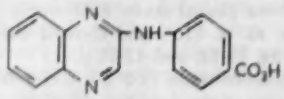
By R. M. Acheson.

Some quinoxaline analogues of pteroic and pteroylglutamic acid have been synthesised. One of these had a small growth-inhibitory effect on *Lactobacillus casei*, prevented by pteroylglutamic acid. 2 : 6 : 7-Trichloroquinoxaline has been prepared and condensed with two amines, but the products had no activity against *Plasmodium gallinaceum*.

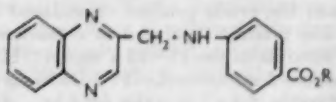
A number of analogues of the growth factors, pteroic and pteroylglutamic acid, have already been prepared [1] and examined biologically. 4-(2-Quinoxalinylcarbonylamino)-benzoylglutamic acid [2] was a pteroylglutamic acid antagonist only with *Lb. casei*. This, the similarity between the quinoxaline and the pteridine ring system, and the report [3] that the growth of *Streptococcus lactis R.*, inhibited by quinoxaline, is restored by excess of pteroylglutamic acid, made it desirable to examine more analogues of pteroic and pteroylglutamic acid.

[1] Acheson, King, and Spensley, *J.*, 1949, 1401, give a summary of earlier literature; see also Fahrenbach, Collins, Hultquist, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 4006, and preceding papers.
[2] Woolley and Pringle, *J. Biol. Chem.*, 1948, **174**, 327.
[3] Hall, *Biochem. J.*, 1946, **40**, xlii.

p-2′-Quinoxalinylaminobenzoic acid (I) was obtained in good yield from 2-chloroquinoxaline and *p*-aminobenzoic acid in *n*-propanol; a subsequent note [4] suggests that none of this product could be obtained from the two reactants under a variety of conditions. The compound did not, however, appreciably affect the growth of *S. lactis R.* 2-Chloroquinoxaline also combined with ethyl *p*-aminobenzoyl-(−)-glutamate, but not with the acid, to give the corresponding 2-aminoquinoxaline. Hydrolysis gave *p*-2′-quinoxalinylaminobenzoyl-(−)-glutamic acid which had a small growth-inhibitory effect on *Lb. casei*, prevented by pteroylglutamic acid.



(I)



(II); R = H (III); R = Et

The preparation of *p*-2′-quinoxalinylmethylaminobenzoic acid (II) was next attempted, and for this it was hoped to prepare 2-bromomethylquinoxaline. Although bromination of 2-methylquinoxaline [5] to tribromomethylquinoxaline [6] was easy attempts to reduce this compound or to stop the bromination at the monosubstitution stage were unsuccessful. Hydroxyiminoacetoacetic ester and *o*-phenylenediamine gave a mixture of 2-methylbenziminazole and 2-hydroxy-3-methylquinoxaline. Disodium ditoluene-*p*-sulphonyl-*o*-phenylenediamine and 1 : 2-dibromopropanol gave the expected condensate, hydrolysed to 1 : 2 : 3 : 4-tetrahydro-2-hydroxymethylquinoxaline. The yields obtainable in the last stage were so variable that this approach was abandoned; also oxidation of this quinoxaline with potassium ferricyanide gave only quinoxaline itself.

Quinoxaline-2-aldehyde reacted with *p*-aminobenzoic acid, or its ethyl ester, to give the anils, subsequently prepared [7,8] by less convenient procedures. In spite of Kjaer's failure [7] to reduce these anils that from the ester was hydrogenated over Adams catalyst to ethyl *p*-2′-quinoxalinylmethylaminobenzoate (III); the analogous reduction of the acid anil to the acid (II) has been described.[8] α-Bromo-β-4-ethoxycarbonylanilinoacraldehyde was now obtained from the corresponding 4-ethoxycarbonylanil hydrobromide by hydrolysis, but all attempts to condense it with *o*-phenylenediamine gave black tars. β-Ethoxycarbonylanilino-α-nitroacraldehyde, from ethyl *p*-aminobenzoate and nitrosodiomalondialdehyde, condensed as expected with *o*-phenylenediamine to give 3-nitro-6 : 7-benzo-1 : 5-diazepine, which was also obtained directly from *o*-phenylenediamine and the nitromalondialdehyde.

2-(2-Diethylaminoethyl)-[9] and 2-(3-diethylaminopropyl)-[9] aminoquinoxalines and their 6 : 7-dichloro-derivatives were found inactive against *P. gallinaceum* in chicks. The analytical data given [9] for the first two quinoxalines suggest that they were hemihydrates; the anhydrous compounds are now described. 2 : 6 : 7-Trichloroquinoxaline, which yielded the corresponding 2-aminoquinoxalines from the appropriate amines, was prepared from 1 : 2-diamino-4 : 5-dichlorobenzene by a four-stage synthesis.

Experimental

p-2′-*Quinoxalinylaminobenzoic Acid.*—*p*-Aminobenzoic acid (0·69 g.) and 2-chloroquinoxaline (0·82 g.) were refluxed in *n*-propanol (6 ml.) for 2 hr.; a yellow powder (1·12 g.) then separated and was crystallised from nitrobenzene forming yellow needles. The *acid* was purified by precipitation from aqueous sodium carbonate by dilute hydrochloric acid, and had m. p. 344—345° (decomp.) (Found, after drying at 150° *in vacuo*: C, 66·3, 66·6; H, 4·4, 4·5; N, 15·5.

[4] Drumheller and Schultz, *J. Amer. Chem. Soc.*, 1955, **77**, 6637.
[5] Borsche and Doller, *Annalen*, 1938, **537**, 39.
[6] Bennett and Willis, *J.*, 1928, 1960.
[7] Kjaer, *Acta Chem. Scand.*, 1948, **2**, 455.
[8] Leese and Rydon, *J.*, 1955, 303.
[9] Crowther, Curd, Davey, and Stacey, *J.*, 1949, 1260.

Calc. for $C_{15}H_{11}O_2N_3.\frac{1}{2}H_2O$: C, 66·6; H, 4·3; N, 15·6%). Drumheller and Schultz [4] give m. p. 340° but no analyses.

Ethyl p-2′-*Quinoxalinylaminobenzoyl*-(−)-*glutamate*.—2-Chloroquinoxaline (0·6 g.) and ethyl *p*-aminobenzoyl-(−)-glutamate (1·18 g.) were refluxed in ethanol (5 ml.) for 4 hr. The brown precipitate (1·3 g., 79%) was crystallised from ethanol (charcoal) giving the *quinoxaline* as yellow-brown needles, m. p. 168° (Found, after drying at 116°/0·5 mm.: C, 64·0; H, 5·5; N, 12·2. $C_{24}H_{26}O_5N_4$ requires C, 64·0; N, 5·8; N, 12·4%).

p-2′-Quinoxalinylaminobenzoyl-(−)-*glutamic acid*.—The ester (0·72 g.) in ethanol (12 ml.) was kept with sodium hydroxide (0·24 g.) in water (2 ml.) at 20° for 90 min. The precipitated sodium salt was dissolved in water and acidified, giving the *acid* which was purified by dissolution in aqueous sodium hydrogen carbonate. Treatment with charcoal and precipitation from the boiling solution by dilute hydrochloric acid gave a yellow-brown powder (0·54 g., 86%), m. p. 252° (decomp.) (Found, after drying at 116°/15 mm.: C, 59·6; H, 4·5; N, 14·0. $C_{20}H_{18}O_5N_4.\frac{1}{2}H_2O$ requires C, 59·6; H, 4·7; N, 13·9%).

NN′-*Ditoluene*-p-*sulphonyl*-o-*phenylenediamine*.—A mixture of toluene-*p*-sulphonyl chloride (59 g.), *o*-phenylenediamine (15 g.), and pyridine (75 ml.) was heated on a water-bath for 1 hr. and then poured into water (1 l.), and the precipitate collected. Crystallisation from ethanol gave the derivative as prisms (46·2 g.), m. p. 204° (Lit.[10] gives m. p. 201—202°).

1 : 2 : 3 : 4-*Tetrahydro*-2-*hydroxymethyl*-1 : 4-*ditoluene*-p-*sulphonylquinoxaline*.—Ditoluene-*p*-sulphonyl-*o*-phenylenediamine (88·2 g.) and 2 : 3-dibromopropanol (46·25 g.) in ethanol (200 ml.) were successively added to a solution from sodium (9·75 g.) and ethanol (1 l.). After refluxing for 6 hr. the solvent was removed and the residual sticky solid washed with water and dried. It was then refluxed with benzene (100 ml.), and after cooling the residue was collected and dissolved in boiling ethanol (1 l.). On cooling the *quinoxaline* (44·5 g.) separated in prisms, m. p. 193° (Found: C, 58·1; H, 5·3; N, 5·7; S, 13·2. $C_{33}H_{34}O_5N_2S_2$ requires C, 58·4; H, 5·1; N, 5·9; S, 13·5%).

1 : 2 : 3 : 4-*Tetrahydro*-2-*hydroxymethylquinoxaline*.—The above derivative (5·08 g.) was dissolved in concentrated sulphuric acid (50 ml.) containing water (0·5 ml.). After 2 days in the warm the solution was poured on ice, basified, and repeatedly extracted with chloroform. Evaporation of the dried extracts gave the *tetrahydroquinoxaline* (1·38 g., 84%), prisms (from ethanol), m. p. 140—141° (Found: C, 65·7; H, 7·3; N, 16·5. $C_9H_{12}ON_2$ requires C, 65·8; H, 7·3; N, 17·1%). The *picrate* separated from water containing a trace of ethanol in yellow prisms, m. p. 179—180° (decomp.) (Found: C, 45·3; H, 4·1. $C_{15}H_{15}O_8N_5$ requires C, 45·6; H, 3·8%). The high yield reported here could never be reproduced. More dilute sulphuric acid failed to produce complete hydrolysis, and increased reaction time gave much lower yields, probably due to sulphonation. Concentrated hydrochloric acid at 170° for 9 hr. gave 46% of the hydroxymethylquinoxaline, m. p. and mixed m. p. 140°.

Potassium ferricyanide (4·8 g.) in water (20 ml.) was added to a solution of the quinoxaline (0·56 g.) and sodium hydroxide (0·7 g.) in water (20 ml.). After 30 min. the solution was filtered and extracted 7 times with chloroform. Evaporation gave a black tar (0·1 g.), from which some quinoxaline, b. p. 130°/10 mm., m. p. 26°, was obtained (Found: C, 73·4; H, 4·8; N, 21·4. Calc. for $C_8H_6N_2$: C, 73·8; H, 4·6; N, 21·5%). Hinsberg [11] gives m. p. 27°.

Methyl Quinoxaline-2-*orthocarboxylate*.—2-Tribromomethylquinoxaline (5·6 g.) was added to methanolic sodium methoxide [from sodium (1·2 g.) and methanol (30 ml.)] and the mixture refluxed for 4½ hr. The solvent was removed *in vacuo*; the residual *ortho-ester*, which solidified on addition of water, separated from methanol in hair-needles, m. p. 63—65° (Found: C, 61·8; H, 6·0; N, 11·7. $C_{12}H_{14}O_3N_2$ requires C, 61·5; H, 6·0; N, 12·0%).

Reaction of Ethyl Hydroxyiminoacetoacetate with o-Phenylenediamine.—(i) The ester (3·2 g.), the diamine (2·16 g.), and acetic acid (1·14 ml.) were refluxed in ethanol (10 ml.) for 5 hr. On cooling, a pale yellow solid (0·25 g., 8%) separated. The filtrate was basified, and the precipitated oil collected with ether and converted into the picrate. 2-Methylbenziminazole picrate (1·8 g., 25%) was obtained, m. p. and mixed [12] m. p. 211—212° (Found: C, 46·2; H, 3·3. Calc. for $C_{14}H_{11}O_7N_5$: C, 46·5; H, 3·0%). The pale yellow solid was soluble in aqueous sodium hydroxide, but not in sodium carbonate solution; crystallisation from ethanol gave 2-hydroxy-3-methylquinoxaline, m. p. 245° (Found: C, 67·2; H, 4·8; N, 17·5. Calc. for $C_9H_8ON_2$: C, 67·5; H, 5·0; N, 17·5%). Lit.[13] gives m. p. 245°.

[10] Reverdin and Crepieux, *Ber.*, 1902, **35**, 314.
[11] Hinsberg, *Ber.*, 1884, **17**, 320.
[12] King and Acheson, *J.*, 1949, 1396.
[13] Ruhemann and Stapleton, *J.*, 1900, 249.

(ii) The diamine dihydrochloride (1·81 g.) and the ester (1·59 g.) in ethanol (15 ml.) were refluxed for 3 hr. Very little material was precipitated on neutralisation, but picric acid gave 2-methylbenziminazole picrate (1·4 g., 39%), m. p. and mixed m. p. 211—212°.

(iii) Refluxing the diamine (1·08 g.), the ester (1·59 g.), and ethanol (7 ml.) for 9 hr. gave 2-hydroxy-3-methylquinoxaline (0·5 g., 31%) and 2-methylbenziminazole [isolated as the picrate (1·2 g., 33%)].

Anils from Quinoxaline-2-aldehyde.—(i) The aldehyde (0·46 g.) and *p*-aminobenzoic acid (0·4 g.) were heated at 100° in dioxan (5 ml.) for 1 hr. The anil rapidly separated as yellow needles (0·72 g., 89%), which were crystallised from dioxan; the anil had m. p. 286—287° (decomp.) (Found: C, 69·6; H, 4·2; N, 14·9. Calc. for $C_{16}H_{11}O_2N_3$: C, 69·3; H, 4·0; N, 15·2%). Lit.[7] gives m. p. 285°. It reacted immediately with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid, and nothing homogeneous could be isolated from attempts to reduce it with sodium amalgam, or with hydrogen over Raney nickel, or palladised charcoal in alkaline solution; hydrogen over Adams catalyst is successful.[8]

(ii) The aldehyde (1·9 g.) and ethyl *p*-aminobenzoate (2·0 g.) were refluxed in dioxan (10 ml.) for 3 hr., the solution was cooled and water added. The *anil* (3·01 g., 82%) separated from aqueous dioxan in very pale yellow needles, m. p. 139° (Found: C, 71·0; H, 4·8; N, 13·6. Calc. for $C_{18}H_{16}O_2N_2$: C, 70·8; H, 4·9; N, 13·8%). Lit.[7] gives m. p. 139°.

Ethyl p-2-Quinoxalinylmethylaminobenzoate.—The last anil (0·527 g.) in dioxan (15 ml.) was hydrogenated at room temperature and pressure over Adams catalyst until the absorption equivalent to one double bond had taken place. Further absorption occurred if permitted. The dark brown solution was filtered and evaporated to dryness *in vacuo*. Treatment of the residual tar with ethanol gave the secondary *amine* (0·188 g., 35%) which was washed with ethanol; it separated from pyridine in prisms, m. p. 229—232° (slight decomp.) (Found: C, 70·0; H, 5·3; N, 13·3%; *M*, 295. $C_{18}H_{17}O_2N_3$ requires C, 70·4; H, 5·5; N, 13·7%; *M*, 307). It was almost insoluble in boiling ethanol, water, and N-aqueous hydrochloric acid, but dissolved in warm aqueous 3—4N-hydrochloric acid, and did not react with 2 : 4-dinitrophenylhydrazine. It gave a dark blue solid with concentrated hydrochloric acid and a dark purple solution in concentrated sulphuric acid which gave a purple precipitate on dilution with water. The original anil was not affected by hydrogen and palladised charcoal, but with Raney nickel in dioxan at room temperature and pressure absorption ceased when 36% of that required to saturate one double bond had been adsorbed, and a 33% yield of the secondary amine was obtained.

α-Bromo-β-4-ethoxycarbonylanilinoacraldehyde 4-Ethoxycarbonylanil.—Ethyl *p*-aminobenzoate (7·5 g.) and αβ-dibromo-β-formylacrylic acid (5·9 g.) were boiled in ethanol (40 ml.) for 20 min. Next day the orange-red precipitate (7·9 g., 62%) was crystallised from aqueous ethanol, giving the *anil hydrobromide dihydrate* as yellow needles, m. p. 249—250° (decomp.) (Found: C, 44·9; H, 4·5; N, 4·9. $C_{21}H_{21}O_4N_2Br,HBr,2H_2O$ requires C, 44·8; H, 4·6; N, 5·0%).

α-Bromo-β-4-ethoxycarbonylanilinoacraldehyde.—The hydrobromide (9·7 g.) was refluxed with water (1·5 l.) for 45 min. Next day the yellow precipitate (5·1 g., 99%) was crystallised from ethanol giving the *acraldehyde* in needles, m. p. 159—160° (Found: C, 48·0; H, 3·8. $C_{12}H_{12}O_3NBr$ requires C, 48·3; H, 4·0%). All attempts to condense this compound with *o*-phenylenediamine in boiling ethanol alone, or in the presence of sodium carbonate or one or two mol. of hydrochloric acid, or in ethylene glycol at 140°, gave intractable black tars.

β-4-Ethoxycarbonylanilino-α-nitroacraldehyde.—A suspension of sodium nitromalondialdehyde (1·39 g.) in water (5 ml.) was added to ethyl *p*-aminobenzoate (1·65 g.) in water (10 ml.) and concentrated hydrochloric acid (1 ml.). After a few minutes on a steam-bath the yellow *acraldehyde* was collected (2·5 g., 95%); it separated from ethanol in needles or prisms, m. p. 158—159° (Found: C, 54·9; H, 4·7; N, 10·4. $C_{12}H_{12}O_5N_2$ requires C, 54·5; H, 4·5; N, 10·6%).

3-Nitro-6 : 7-benzo-1 : 5-diazepine.—(i) The above anil (0·88 g.) and *o*-phenylenediamine (0·36 g.) were refluxed in ethanol (5 ml.). A red solid was precipitated and, after the addition of more ethanol (15 ml.), heating was continued for 1 hr. The red *benzodiazepine* (0·51 g., 81%) was collected and ethyl *p*-aminobenzoate (0·37 g., 67%) recovered from the filtrate. The benzodiazepine was practically insoluble in dilute acids or alkalis and the usual common solvents. It dissolved in concentrated sulphuric acid to a yellow solution which charred when heated and it separated from quinoline, the only effective solvent, in dark red prisms which did not melt nor discolour at 360° (Found, after drying at 144° *in vacuo* over P_2O_5: C, 57·1; H, 3·5; N, 22·2. $C_9H_7O_2N_3$ requires C, 57·1; H, 3·8; N, 22·2%).

(ii) Sodium nitromalondialdehyde (0·32 g.), *o*-phenylenediamine (0·25 g.), concentrated

hydrochloric acid (0·25 ml.), and water (6 ml.) were heated for 30 min. on a steam-bath. The yellow precipitate rapidly became red (0·31 g., 71%) and had the same properties as the benzodiazepine described above (Found : C, 57·4; H, 3·6%).

Ethyl 6 : 7-*Dichloro*-2-*hydroxyquinoxaline*-3-*carboxylate*.—1 : 2-Dichloro-4 : 5-dinitrobenzene (4·74 g.) was hydrogenated in ethanol (30 ml.) over Raney nickel until the theoretical absorption for two nitro-groups had taken place. The mixture, without filtration as the diamine oxidised very rapidly in air, was poured into boiling ethanol (20 ml.) containing ethyl mesoxalate (3·8 g.) and refluxing was continued for 45 min. The mixture was treated with charcoal and filtered whilst hot. Crystallisation of the product (3·7 g.) from ethyl acetate gave the *ester* as pale green needles, m. p. 230° (Found : C, 46·1; H, 2·9; N, 9·8; Cl, 24·8. $C_{11}H_8O_3N_2Cl_2$ requires C, 46·0; H, 2·8; N, 9·8; Cl, 24·7%).

6 : 7-*Dichloro*-2-*hydroxyquinoxaline*-3-*carboxylic Acid*.—The ester (5·1 g.) was heated on a steam-bath with 2N-sodium hydroxide for 1 hr., water (50 ml.) was added, and the mixture was boiled and filtered into concentrated hydrochloric acid (50 ml.). The *quinoxalinecarboxylic acid* (4·5 g.) separated from ethanol in yellow needles, m. p. 340° (decomp.) (Found : C, 41·9; H, 1·5; Cl, 27·2. $C_9H_4O_3N_2Cl_2$ requires C, 41·7; H, 1·5; Cl, 27·4%).

6 : 7-*Dichloro*-2-*hydroxyquinoxaline*.—The acid (6·1 g.) was refluxed in nitrobenzene (60 ml.) until carbon dioxide was no longer evolved. After cooling light petroleum (200 ml.; b. p. 60—80°) was added and the *quinoxaline* (4·95 g.) then precipitated. It was washed with light petroleum and crystallised from *n*-propanol forming prisms, m. p. 343° (decomp.) (Found : C, 44·5; H, 1·9. $C_8H_4ON_2Cl_2$ requires C, 44·7; H, 1·9%).

2 : 6 : 7-*Trichloroquinoxaline*.—The hydroxyquinoxaline (1·0 g.) was refluxed with phosphoryl chloride (10 ml.) for 45 min. and the resulting dark red solution evaporated to dryness *in vacuo*. Water was added and the residue repeatedly extracted with ether. Evaporation of the dried (Na_2SO_4) extracts gave the *trichloroquinoxaline* (1·0 g.) as pale pink needles (from ethanol), m. p. 147° (Found : C, 40·9; H, 1·4; N, 11·5; Cl, 44·7. $C_8H_3N_2Cl_3$ requires C, 41·1; H, 1·3; N, 12·0; Cl, 45·6%).

6 : 7-*Dichloro* - 2 - 2′ - *diethylaminoethylaminoquinoxaline*.—2 : 6 : 7 - Trichloroquinoxaline (0·35 g.) was heated with 2-diethylaminoethylamine (1 ml.) to 110—140° for 3 hr. and excess of amine was then removed at 100°/14 mm. The residual oil was dissolved in dilute acid, the solution extracted with ether, the aqueous layer basified, and the *quinoxaline* collected with ether. It was a pale yellow oil, b. p. 168—173° (bath temp.)/0·03 mm. (Found : N, 18·7. $C_{14}H_{18}N_4Cl_2$ requires N, 17·9%). The picrate was very difficult to purify, but the highly crystalline *monomethiodide* separated from ethanol in prisms, m. p. 196—197° (Found : C, 39·5; H, 4·7; N, 12·1. $C_{15}H_{21}N_4Cl_2I$ requires C, 39·6; H, 4·6; N, 12·3%).

6 : 7-*Dichloro*-2-3′-*diethylaminopropylaminoquinoxaline*.—This (1·15 g.) was obtained in the same way from 2 : 6 : 7-trichloroquinoxaline (1·2 g.) and 3-diethylaminopropylamine (3·2 ml.), and distilled as a pale yellow oil, b. p. 183—188°(bath. temp.)/0·05 mm. It solidified after the second distillation and crystallised from ether in prisms, m. p. 84—86° (Found : Cl, 20·9. $C_{15}H_{20}N_4Cl_2$ requires Cl, 21·7%). The *picrate* separated from ethanol in orange prisms, m. p. 182° (Found : C, 45·6; H, 4·2; N, 17·2. $C_{21}H_{23}O_7N_7Cl_2$ requires C, 45·3; H, 4·1; N, 17·6%). The *monomethiodide* separated from ethanol in pale brown prisms, m. p. 212° (decomp.) (Found : C, 40·8; H, 5·0; N, 11·4. $C_{16}H_{23}H_4Cl_2I$ requires C, 40·9; H, 4·9; N, 11·9%).

2-2′-*Diethylaminoethylaminoquinoxaline*.—This was obtained (72% yield) similarly and had b. p. 140°/0·02 mm. (Found : C, 69·2; H, 8·6. $C_{14}H_{20}N_4$ requires C, 68·8; H, 8·2%). The dipicrate had m. p. 185° (sinters 183°) (Found : C, 44·4; H, 3·8; N, 19·7. Calc. for $C_{26}H_{26}O_{14}N_{10}$: C, 44·4; H, 3·7; N, 19·9%). Lit.[9] gives b. p. 135°/0·1 mm. and m. p. 183—185°, respectively.

2-3′-*Diethylaminopropylaminoquinoxaline*.—This was also prepared similarly and had b. p. 200—205°/0·1 mm. (Found : C, 69·8; H, 8·8; N, 20·9. $C_{15}H_{22}N_4$ requires C, 69·8; H, 8·5; N, 21·7%). The dipicrate, orange prisms which change to yellow needles, from ethanol, had m. p. 164° (Found : C, 44·8; H, 4·0; N, 18·9. Calc. for $C_{27}H_{28}O_{14}N_{10}$: C, 45·2; H, 3·9; N, 19·5%). Lit.[9] gives b. p. 153°/0·1 mm. and m. p. 127—129° (different crystalline form ?), respectively.

Dr. R. H. Nimmo Smith and Miss I. Tonkin are thanked for the biological data, and Dr. F. E. King, F.R.S., for much advice and encouragement.

Department of Biochemistry, Oxford University. [*Received, June 18th*, 1956.]

925. *Kinetics of the Decarboxylation of Oxaloacetic Acid.*

By E. Gelles.

The kinetics of decarboxylation of oxaloacetic acid in aqueous solution have been studied at 25°, 30°, and 37° over a range of pH. Arrhenius parameters are obtained for the first-order decomposition of oxaloacetic acid and of its univalent anion. The kinetics of decarboxylation of other β-keto-carboxylic acids are discussed.

The relative rates of decarboxylation of acids and their anions are now known for a number of β-keto-carboxylic acids. The considerable variation in these relative reactivities is produced by an interplay of energy and entropy factors, an analysis of which could throw further light on the reaction mechanism. Kinetic data for an acid and its anion have been reported at more than one temperature only for malonic acid.[1,2] The kinetics of the decarboxylation of oxaloacetic acid have been studied in detail at 37°.[3] This reaction is of interest for several reasons, *e.g.*, catalysis by paramagnetic ions [4] and carbon-isotope effects.[5] Arrhenius parameters have now been obtained for the first-order decarboxylation of oxaloacetic acid and of its univalent anion.

Experimental

Weighed samples of oxaloacetic acid (Found, by titration against alkali: *M*, 132·5. Calc. for $C_4H_4O_5$: *M*, 132·1) were dissolved in the requisite amounts of water, standard hydrochloric acid, and potassium chloride solutions. The apparatus and experimental procedure have been described previously.[4] Kinetic measurements were made in a water thermostat controlled to ±0·01°. "AnalaR" materials and "grade A" volumetric glassware were used.

Results

Pedersen has shown that oxaloacetic acid and its two anions separately undergo first-order decarboxylation to pyruvic acid.[3] The observed first-order rate coefficient for the total reaction, $k_{obs.}$, is related to the separate rate constants for the acid, k_0, for the univalent anion, k_1, and for the bivalent anion, k_2:

$$k_{obs.} = k_0 + (k_1 - k_0)\alpha_1 + (k_2 - k_0)\alpha_2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where α_1 and α_2 are the degrees of ionisation to univalent and bivalent ions, respectively. Pedersen has determined the ionisation constants of oxaloacetic acid, K_1 and K_2, (and of the decomposition product, pyruvic acid) as a function of ionic strength at 25° and 37°.[6] The required ionisation constants for 30° have been calculated from these data:

$$\begin{aligned}
\text{at } 25°: \quad & -\log K_1 = 2{\cdot}555 - 1{\cdot}013I^{\frac{1}{2}} + 0{\cdot}75I; \\
& -\log K_2 = 4{\cdot}370 - 2{\cdot}026I^{\frac{1}{2}} + 1{\cdot}57I \\
\text{at } 30°: \quad & -\log K_1 = 2{\cdot}511 - 1{\cdot}023I^{\frac{1}{2}} + 0{\cdot}80I; \\
& -\log K_2 = 4{\cdot}365 - 2{\cdot}047I^{\frac{1}{2}} + 1{\cdot}60I \\
\text{at } 37°: \quad & -\log K_1 = 2{\cdot}450 - 1{\cdot}038I^{\frac{1}{2}} + 0{\cdot}86I; \\
& -\log K_2 = 4{\cdot}359 - 2{\cdot}076I^{\frac{1}{2}} + 1{\cdot}65I \quad . \quad . \quad . \quad . \quad . \quad (2)
\end{aligned}$$

For a given mixture the degrees of ionisation, α_1 and α_2, and the ionic strength, I, are calculated from equations (2)—(5), where HA^- and A^{2-} represent the univalent and bivalent anions of oxaloacetic acid, respectively:

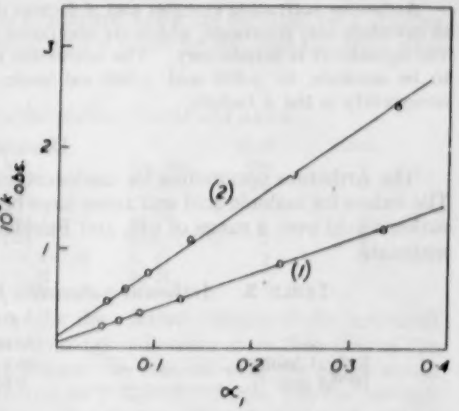
$$\alpha_1/(1 - \alpha_1 - \alpha_2) = K_1/[H^+]; \quad \alpha_2/(1 - \alpha_1 - \alpha_2) = K_1K_2/[H^+]^2 \quad . \quad (3), (4)$$

$$I = \tfrac{1}{2}([H^+] + [K^+] + [Cl^-] + [HA^-] + 4[A^{2-}]) \quad . \quad . \quad . \quad . \quad (5)$$

---

[1] Hall, *J. Amer. Chem. Soc.*, 1949, **71**, 2691.
[2] Fairclough, *J.*, 1938, 1186.
[3] Pedersen, *Acta Chem. Scand.*, 1952, **6**, 285.
[4] Gelles and Clayton, *Trans. Faraday Soc.*, 1956, **52**, 353.
[5] Gelles and Reed, *Nature*, 1955, **176**, 1262.
[6] Pedersen, *Acta Chem. Scand.*, 1952, **6**, 243.

Kinetic measurements have now been made at three temperatures. For a given oxaloacetic acid concentration, experiments were carried out at a number of hydrochloric acid concentrations, so that the sum of the hydrochloric acid and potassium chloride concentrations was 0·100. At the concentrations of mineral acid used the bivalent anion made a very small contribution to the total rate of reaction. The experiments at 37° gave values of k_0 and k_1 slightly higher than those generally found by Pedersen, but in excellent agreement with his data for similar oxaloacetic acid concentrations.[3] The results of typical experiments at 25° and 30° for one oxaloacetic acid concentration are summarised in Table 1. Concentrations are quoted in moles/l. and first-order rate coefficients in min.$^{-1}$ units. The oxaloacetic acid



Variation of first-order rate coefficients with degree of ionisation of oxaloacetic acid. Plots of $10^3 k_{obs.}$ against α_1, (1) at 25°, (2) at 30°.

concentration is 0·0294. It is seen that agreement between observed and calculated rate coefficients would not be adversely affected by neglecting the very small contribution to the rate of the bivalent anion. Preliminary values of k_0 and k_1 were obtained graphically on this basis. Neglecting the term due to the bivalent anion in equation (I), we have

$$k_{obs.} = k_0 + (k_1 - k_0)\,\alpha_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The Figure shows plots of $k_{obs.}$ against α_1. The observed rate coefficients are obtained from first-order Guggenheim plots covering four half-times of reaction, and are accurate to ±1—2%. The first-order rate law is obeyed for the total reaction to a very good approximation essentially

TABLE 1. *Decarboxylation of acid and anion.*

Temp.	[HCl]	[KCl]	I	α_1	α_2	$10^3 k_{obs.}$	$10^3 k_{calc.}$
25°	0·000	0·100	0·1098	0·3342	0·0046	1·17	1·19
,,	0·010	0·090	0·1067	0·2284	0·0018	0·84	0·829
,,	0·030	0·070	0·1037	0·1275	0·0005	0·490	0·490
,,	0·050	0·050	0·1025	0·0855	0·0002	0·350	0·350
,,	0·070	0·030	0·1019	0·0640	0·0001	0·273	0·278
,,	0·100	0·000	0·1014	0·0463	0·00006	0·221	0·219
			$10^3 k_0 = 0·064$, $10^3 k_1 = 3·40$ ($10^3 k_2 \sim 1$)				
30°	0·000	0·100	0·1102	0·3473	0·0047	2·40	2·41
,,	0·010	0·090	0·1071	0·2417	0·0019	1·71	1·72
,,	0·030	0·070	0·1040	0·1377	0·0005	1·06	1·04
,,	0·050	0·050	0·1027	0·0933	0·0002	0·745	0·745
,,	0·070	0·030	0·1020	0·0700	0·0001	0·591	0·592
,,	0·100	0·000	0·1015	0·0507	0·00007	0·472	0·466
			$10^3 k_0 = 0·134$, $10^3 k_1 = 6·67$ ($10^3 k_2 \sim 2$)				
37°			$10^3 k_0 = 0·345$, $10^3 k_1 = 15·4$, $10^3 k_2 = 4·2$				

because the ionisation constants of oxaloacetic acid and the decomposition product, pyruvic acid, are nearly equal.[3] The values of α_1 and α_2 given in Table 1 are calculated for the beginning of the reaction: their variation during the course of the reaction is inappreciable. The values

of k_0 are accurate to ±3—4%, those of k_1 to ±1—2%. The values of $k_{calc.}$ listed in Table 1 are calculated from the final values of k_0, k_1, and k_2.

TABLE 2. *Observed and calculated rate constants.*

$k_0 = 5{\cdot}13 \times 10^{14} \cdot \exp(-25{,}800/RT)$, $k_1 = 2{\cdot}87 \times 10^{14} \cdot \exp(-23{,}100/RT)$ min.$^{-1}$.

		25°		30°		37°	
		obs.	calc.	obs.	calc.	obs.	calc.
Acid	10^3k_0	0·064	0·065	0·134	0·132	0·345	0·347
Anion	10^3k_1	3·40	3·44	6·67	6·57	15·4	15·4

Arrhenius activation energies and A factors derived from the experimental results are used to calculate rate constants, which are compared with the observed rate constants in Table 2. The agreement is satisfactory. The activation energies for the acid and anion are considered to be accurate to ±500 and ±300 cal./mole, respectively, and there is a corresponding uncertainty in the A factors.

DISCUSSION

The Arrhenius parameters for oxaloacetic and malonic acids are compared in Table 3. The values for malonic acid and anion have been evaluated from Hall's data [1] (80—90°) on malonic acid over a range of pH, and Fairclough's data [2] (76—120°) on sodium hydrogen malonate.

TABLE 3. *Arrhenius parameters for oxaloacetic and malonic acids.*

	Oxaloacetic		Malonic	
	Acid	Anion	Acid	Anion
E (kcal./mole)	25·8	23·1	30·8	27·9
$10^{-13}A$ (sec.$^{-1}$)	0·85	0·48	5·5	0·0098

For both compounds the anion has a lower activation energy for decarboxylation than has the acid. The pre-exponential A factors are around 10^{13} sec.$^{-1}$, except for the malonate ion. For malonic acid and the malonate ion the ratio of A factors is about 600. Malonic acid reacts 10 times faster than its anion at 90° (~4 times faster at 30°), as the entropy factor outweighs the energy factor. In oxaloacetic acid, where this entropy effect is absent, the anion is 50 times more reactive than the undissociated acid at 30°.

Oxaloacetic acid can form two univalent ions (I) and (II).

(I) $H_2OC{\cdot}CO{\cdot}CH_2{\cdot}CO_2^-$ $\qquad$ $^-O_2C{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$ (II)

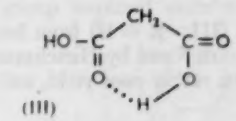
A comparison of the ionisation constants of pyruvic, oxaloacetic, and acetoacetic acid confirms that the univalent oxaloacetate ion is predominantly (II). However, evidence is available that (I) is very much more reactive than (II).[7] Structure (II) would indeed be expected to be less reactive than the un-ionised acid; the major contribution to the rate of decarboxylation of the anion may be taken to come from structure (I). In that case, the A factor for structure (I) will be greater than the experimental value given in Table 3 by a factor depending on the equilibrium concentrations of (I) and (II).

The most probable conformations of malonic acid and anion are the hydrogen-bonded forms (III) and (IV). In malonic acid (III) a proton must be transferred from one carboxyl group to another for decarboxylation to occur. Malonic acid will therefore react in its most probable conformation and show a normal A factor of about 10^{13} sec.$^{-1}$. In the malonate ion (IV) decarboxylation is possible without proton transfer if the carboxyl group (*b*) is eliminated preferentially, as might be expected by analogy with the oxaloacetate ion. The malonate ion might then react by way of an energetically easier path with the carboxyl groups twisted out of the plane of the carbon skeleton. The observed low A factor may be associated with this less probable conformation.

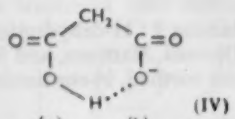
The differences in the activation energies of acid and anion for oxaloacetic and malonic acid, and for other β-keto-carboxylic acids are most easily interpreted in terms of the electronic effect of substituent groups on the stability of the activated complex, to which

[7] Steinberger and Westheimer, *J. Amer. Chem. Soc.*, 1951, **73**, 429.

the enol $HO{\cdot}CX{:}CY_2$ or ion $^-O{\cdot}CX{:}CY_2$ is a contributing structure. Electrophilic groups will stabilise the ion more than the enol, and electron-releasing groups are expected to act in the reverse manner.



(III)



(a) (b) (IV)

In Table 4 relative rates of decarboxylation of acid and anion are collected for a number of β-keto-acids.[8,9] The relative rate for malonic acid is given for 30°, and the other data are for temperatures in the range 18—45°

TABLE 4. *Relative rates of decarboxylation of acid and anion.*

Compound	X	Y	Acid	Anion
αα-Dimethylacetoacetic acid	Me	Me, Me	200	1
Acetoacetic acid	Me	H, H	50	1
Malonic acid	OH	H, H	4	1
Phenylmalonic acid	OH	H, Ph	1	3
Dibromomalonic acid	OH	Br, Br	1	> 1
Acetonedicarboxylic acid	$CH_2{\cdot}CO_2H$	H, H	1	3
Oxaloacetic acid	CO_2H	H, H	1	50

As substituent groups become more electrophilic the relative stability of the activated complex of the anion increases and the activation energy is lowered more than that of the acid, so that the relative rate of the anion increases. In malonic acid the anion would then be expected to have a lower activation energy, as is indeed the case, but the entropy effect causes the acid to react more rapidly. Increasing electrophilic substitution increases the difference in activation energies of acid and anion until this effect overcomes the entropy effect, and leads to the anion's reacting faster than the acid.[9]

My thanks are due to Mr. A. S. Scott for some preliminary measurements.

CHEMISTRY DEPARTMENT, THE UNIVERSITY, GLASGOW. [*Received, June 26th*, 1956.]

[8] Brown, *Quart. Reviews*, 1951, **5**, 131.
[9] Gelles, *J. Amer. Chem. Soc.*, 1953, **75**, 6199.

---

926. *By-ways of Synthesis of Cortisone from Hecogenin. Part I. 9 : 11-Dehydrohecogenin as Intermediate in Preparation of 11-Oxygenated Compounds (11-Oxotigogenin and 3β-Acetoxy-17α-hydroxyallopregnane-11 : 20-dione).*

By R. K. CALLOW and V. H. T. JAMES.

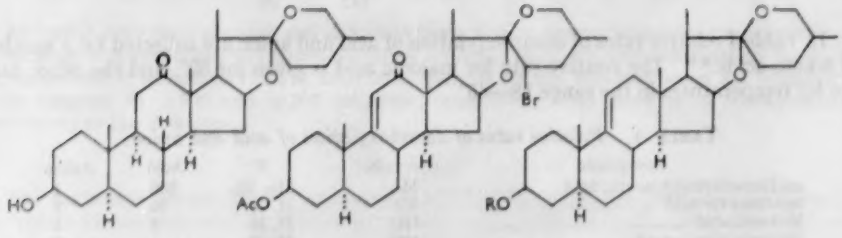
9 : 11-Dehydrohecogenin can be reduced to 9 : 11-dehydrotigogenin, which, by way of the 9 : 11-bromohydrin, yields 11-oxotigogenin. By another route, degradation of 9 : 11-dehydrotigogenin to 3β-acetoxy*allo*-pregna-9(11) : 16-dien-20-one was carried out, and by a series of reactions, again through a 9 : 11-bromohydrin, 3β-acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione was prepared. 11β-Acetoxy-compounds in this series have been prepared, but are not possible intermediates in the synthesis of cortisol.

THE many stages of the known routes for the partial synthesis of cortisone from hecogenin [1] can be accomplished in different orders and by different means; some of these other routes have now been explored. In this paper we describe a method of introducing an oxygen atom at $C_{(11)}$ which can be applied at either the sapogenin stage or the pregnane stage and

[1] For references see Cameron, Evans, Hamlet, Hunt, Jones, and Long, *J.*, 1955, 2807.

provides another practical method for bringing about the change from 12-oxo- to 11-oxo-compounds.[2-5] This is essentially the series of reactions applied by Hicks and Wallis [6] who obtained methyl 3α-acetoxy-11-oxocholanate from methyl 3α-acetoxy-9(11)-cholenate in very poor yield.

Methods for obtaining 9 : 11-dehydrotigogenin (III; R = H) from hecogenin (I) have been described by Djerassi, Martinez, and Rosenkranz [7] and by Hirschmann, Snoddy, and Wendler.[8] The latter method, in our hands, gave a rather poor yield, and we devoted our



(I) (II) (III)

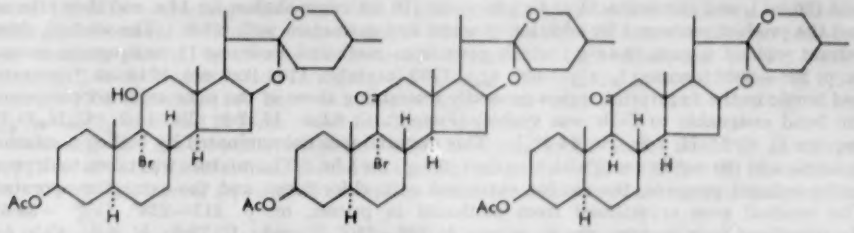
attention to improving the yields of the four stages of the former method. Hecogenin acetate is conveniently brominated in benzene, and the product treated directly with boiling collidine gave 23-bromo-9 : 11-dehydrohecogenin acetate (II) in an over-all yield of 71%. The described [2] method of debromination with zinc in acetic acid went rather slowly, and loss of αβ-unsaturated ketone occurred, but reduction with a zinc–copper couple gave 81% of 9 : 11-dehydrohecogenin acetate. Removal of the 12-oxo-group by preparing a thioketal with ethanedithiol or 3-hydroxypropane-1 : 2-dithiol followed by treatment with Raney nickel gave yields of 40 and 37%, respectively, but reduction by the Huang-Minlon modification of the Wolff–Kishner reaction and reacetylation of the crude product gave 9 : 11-dehydrotigogenin acetate (III; R = Ac) in 75% yield. Two routes in continuance of the synthesis were then followed. In the first, 9 : 11-dehydrotigogenin acetate was converted by *N*-bromoacetamide into the 9 : 11-bromohydrin (IV) which, by oxidation to the 9α-bromo-11-oxo-compound (V) and removal of bromine yielded 11-oxotigogenin acetate (VI).

The second route was the degradation of 9 : 11-dehydrotigogenin by way of the ψ-compound and oxidation to 3β-acetoxy*allo*pregna-9(11) : 16-dien-20-one, which was obtained in a yield of 77%. The 9(11)-ethylenic linkage was inert to oxidation by chromium trioxide under the conditions used. As both ethylenic linkages were attacked by per-acids, the preferred path was by preparation of the 16 : 17-epoxide by the action of alkaline hydrogen peroxide, conversion into the 16-bromo-17α-hydroxy-compound, and debromination with Raney nickel to give 3β-acetoxy-17α-hydroxy*allo*pregn-9(11)-en-20-one (cf. ref. 9). Hypobromous acid was then added to the 9(11)-ethylenic linkage, and oxidation and debromination yielded the known 3β-acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione. Both this compound and 11-oxotigogenin have already been used as intermediates in the synthesis of cortisone : a route to the biologically active 9α-halogeno-compounds is also opened by way of the 9 : 11-bromohydrin of the pregnene.

Concurrently with this work, an investigation was made of a synthesis of cortisol with a protected 11β-hydroxyl group introduced at an earlier stage, rather than obtained at the

[2] Djerassi, Martinez, and Rosenkranz, *J. Org. Chem.*, 1951, **16**, 303.
[3] Cornforth, Osbond, and Phillipps, *J.*, 1954, 907.
[4] Schmidlin and Wettstein, *Helv. Chim. Acta*, 1953, **36**, 1241.
[5] Chapman, Elks, and Wyman, *Chem. and Ind.*, 1955, 603.
[6] Hicks and Wallis, *J. Biol. Chem.*, 1946, **162**, 641.
[7] Djerassi, Martinez, and Rosenkranz, *J. Org. Chem.*, 1951, **16**, 1278.
[8] Hirschmann, Snoddy, and Wendler, *J. Amer. Chem. Soc.*, 1953, **75**, 3252.
[9] Julian, Meyer, Karpel, and Waller, *ibid.*, 1950, **72**, 5145.

end by reduction of the 11-oxo-group of cortisone. Normal acetylation of 11β-hydroxytigogenin yielded only a monoacetate,[9] but under forcing conditions (cf. Turner [10] and Huang-Minlon *et al.*[11]) a 3β : 11β-diacetate was obtained. However, hydrolysis of the 11β-acetoxyl group required such vigorous treatment with methanolic alkali that no



compound in the later stages of the synthesis would be likely to survive. In fact, 11β-hydroxytigogenin could be recovered from its diacetate, but 3β : 11β-diacetoxy-16 : 17-epoxy*allo*pregnan-20-one was broken down to unidentifiable products when an attempt was made to remove both acetyl groups. In the meantime, it has been shown [12,13] that 11β-formylation or 11β-trifluoroacetylation can be usefully employed in analogous series of reactions.

Experimental

M. p.s were determined in a Kofler apparatus with polarised light, and are corrected. Optical rotations were determined in chloroform solutions of concentrations within the limits 0·5—1·0%. Infrared absorption was measured with a double-beam instrument with a rock-salt prism (Perkin–Elmer Model 21), KBr or KCl discs being used unless otherwise stated.

23-*Bromo*-9 : 11-*dehydrohecogenin Acetate*.—Hecogenin acetate (25 g.) was brominated as described by Elks *et al.*[14] and the crude product boiled with collidine for 2 hr. The mixture was diluted with chloroform (250 ml.), and washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water. Evaporation and treatment of the residue with methanol (150 ml.) yielded crude 23-bromo-9 : 11-dehydrohecogenin acetate (20·4 g.), m. p. 219—221° (decomp.), $\lambda_{max.}$ 238 mμ (log ε 4·12, in EtOH).

9 : 11-*Dehydrohecogenin Acetate*.—The bromo-derivative (6·2 g.) was dissolved in a mixture of dioxan (25 ml.) and industrial spirit (95% ethanol + 5% methanol) (225 ml.). To this was added a zinc–copper couple prepared from 30 g. of zinc, and the mixture was boiled under reflux for 8 hr. The solution was filtered, evaporated to half bulk, and then poured into water. The precipitate was taken up in chloroform; drying and evaporation left a residue which, after being boiled with methanol, yielded 9 : 11-dehydrohecogenin acetate (4·27 g.), m. p. 215—218°, $[\alpha]_D$ −10°, $\lambda_{max.}$ 238 mμ (log ε 4·18, in MeOH).

9 : 11-*Dehydrotigogenin Acetate*.—9 : 11-Dehydrohecogenin acetate (4·5 g.), ethylene glycol (105 ml.), and hydrazine hydrate (90%; 3 ml.) were boiled for 1 hr. To the cooled mixture potassium hydroxide (9·2 g.) in water (10 ml.) was added and the mixture was boiled for 20 min.; the condenser was then removed and water boiled off until the temperature of the mixture reached 197°. The condenser was then replaced and refluxing continued for 2½ hr. The mixture was cooled, acidified, and extracted with chloroform. The extract, washed and evaporated, gave a residue which was treated with acetic anhydride (10 ml.) and pyridine (10 ml.) for ½ hr. at 100°. The residue after evaporation was purified by chromatography on alumina. Benzene–light petroleum (b. p. 80—100°) (1 : 9) eluted 9 : 11-dehydrotigogenin acetate, m. p. 199—202·5° (from ethanol), $[\alpha]_D^{21}$ −57°; the yield was 2·75 g. (65% of theory), and 0·4 g. was obtained as a second crop.

[10] Turner, *J. Amer. Chem. Soc.*, 1952, **74**, 4220.
[11] Huang-Minlon, Wilson, Wendler, and Tischler, *ibid.*, p. 5394.
[12] Oliveto, Gerold, and Hershberg, *Arch. Biochem. Biophys.*, 1954, **49**, 244.
[13] Lardon and Reichstein, *Helv. Chim. Acta*, 1954, **37**, 443.
[14] Elks, Phillipps, Walker, and Wyman, *J.*, 1956, 4330.

11-*Oxotigogenin Acetate*.—**9 : 11**-Dehydrotigogenin acetate (0·5 g.) was dissolved in dioxan (70 ml.), water (15 ml.) added, and the solution filtered. *N*-Bromoacetamide (0·2 g.) was added, the flask was covered to exclude light, and 10% aqueous perchloric acid (4 ml.) was added. The mixture was shaken for 5 min., diluted with water to a volume of 250 ml., and kept at 5° for 30 min.; the precipitate was washed with water and dried *in vacuo*. This bromohydrin, acetic acid (30 ml.), and chromic acid (0·4 g.) in water (10 ml.) were shaken for 1 hr. and then filtered, and the product recovered by addition of water and extraction with ether. The washed, dried extract yielded a gum (0·44 g.) which gave from methanol **9α-*bromo*-11-*oxotigogenin acetate***, m. p. 201—206° (decomp.), $[\alpha]_D$ +60°, $\nu_{max.}$ 1730 (acetate), 1708 (ketone), 1248 cm.$^{-1}$ (acetate) and bands in the fingerprint region generally resembling those of the unbrominated compound (no band assignable to C–Br was visible) (Found: C, 63·4; H, 7·9; Br, 14·2. $C_{29}H_{45}O_6Br$ requires C, 63·2; H, 7·9; Br, 14·3%). This material was debrominated by boiling a solution in acetic acid (60 mg. in 2 ml.) with zinc dust (0·5 g.) for 1 hr. The mixture was taken to dryness under reduced pressure, the residue extracted with chloroform, and the extract evaporated. The residual gum crystallised from methanol in prisms, m. p. 217—228°, $[\alpha]_D^{22}$ −38·5°. Recrystallised from acetone, the m. p. rose to 222—230° (Found: C, 73·6; H, 8·9. Calc. for $C_{29}H_{44}O_6$: C, 73·7; H, 9·4%); the infrared absorption was identical with that of an authentic specimen of 11-oxotigogenin acetate.

3β-*Acetoxy*allo*pregna*-9(11) : 16-*dien*-20-*one*.—**9 : 11**-Dehydrotigogenin acetate was prepared by boiling **9 : 11**-dehydrotigogenin acetate with octanoic acid [15] and acetylating the product (3·6 g.). The acetate, without purification, was oxidised directly by adding to its acetic acid solution (35 ml.) a solution (35 ml. of 4·5%) of chromic acid in 90% acetic acid. After ¾ hr. water was added and the solution extracted with ether. The extract was evaporated and the residue dissolved in benzene (40 ml.) and light petroleum (b. p. 40—60°) (50 ml.) and treated with alumina (50 g.). After 2 hr. the alumina was removed and the filtrate evaporated. The product yielded 3β-acetoxy*allo*pregna-9(11) : 16-dien-20-one, m. p. 171—173° (from methanol), $[\alpha]_D$ +101°, $[\alpha]_{5461}$ +124°, $\lambda_{max.}$ 238 mμ (log ε 3·95, in MeOH), $\nu_{max.}$ 1730 (acetate), 1660 (ketone), 1592 (double bond), 1250 (acetate), 823 (double bond) cm.$^{-1}$ (Found: C, 77·1; H, 9·6. Calc. for $C_{23}H_{32}O_3$: C, 77·5; H, 9·1%). Djerassi *et al.*[7] give m. p. 164—166°, $[\alpha]_D^{20}$ +67°, $\lambda_{max.}$ 238 mμ (log ε 4·07), $\nu_{max.}$ 1739, 1672, and 1239 cm.$^{-1}$.

3β-*Acetoxy*-16 : 17-*epoxy*allo*pregn*-9(11)-*en*-20-*one*.—To 3β-acetoxy*allo*pregna-9(11) : 16-dien-20-one (0·27 g.) in ethanol (60 ml.) was added hydrogen peroxide (30%; 2 ml.) and 2N-sodium hydroxide (2 ml.). After 48 hr. at 3° water was added and the precipitate (0·18 g.; m. p. 180—205°) was acetylated. **3β-*Acetoxy*-16 : 17-*epoxy*allo*pregn*-9(11)-*en*-20-*one*** had m. p. 208—212° (from methanol), $[\alpha]_D$ +88° (Found: C, 73·9; H, 8·8. $C_{23}H_{32}O_4$ requires C, 74·2; H, 8·7%), $\nu_{max.}$ 3400 (hydroxyl), 1735 (acetate), 1705 (ketone), 1248 (acetate), 860 (epoxide), 815 cm.$^{-1}$ (double bond). A band at 1300 cm.$^{-1}$ seems to be peculiar to this and the unesterified compound (obtained in impure form).

3β-*Acetoxy*-16-*bromo*-17α-*hydroxy*allo*pregn*-9(11)-*en*-20-*one*.—The epoxy-acetate (0·1 g.) in acetic acid (5 ml.) was treated with 48% hydrobromic acid (2 drops). After 12 hr. the solution was poured into water. The precipitate, when crystallised from aqueous methanol, yielded **3β-*acetoxy*-16-*bromo*-17α-*hydroxy*allo*pregn*-9(11)-*en*-20-*one*** as silvery plates (60 mg.), m. p. 180—184°, $[\alpha]_D$ +8° (Found: C, 60·8; H, 7·5; Br, 17·9. $C_{23}H_{33}O_4Br$ requires C, 60·9; H, 7·35; Br, 17·7%).

3β-*Acetoxy*-17α-*hydroxy*allo*pregn*-9(11)-*en*-20-*one*, obtained by boiling the bromohydrin (550 mg.) for 3 hr. in ethanol (25 ml.) with Raney nickel (3 g.), formed silvery plates (from ethanol), m. p. 198·5—200·5°, $[\alpha]_D^{23}$ −15° (Found: C, 73·4; H, 8·9. $C_{23}H_{34}O_4$ requires C, 73·7; H, 9·13%), $\nu_{max.}$ 1710, with shoulder at 1720 (ketone and acetate), 1260 (acetate), 816 cm.$^{-1}$ (double bond).

3β-*Acetoxy*-9α-*bromo*-17α-*hydroxy*allo*pregnane*-11 : 20-*dione*.—The pregnenone (0·43 g.) was dissolved in dioxan (60 ml.) and water (16 ml.), and *N*-bromoacetamide (0·215 g.) and 1% aqueous perchloric acid (4 ml.) were added successively. The flask was protected from light and shaken for 5 min., and water added to a volume of 250 ml. After ½ hr. at 5° the precipitate was dried [0·1 g., m. p. 155—162° (decomp.), $\nu_{max.}$ 3460 (s) (hydroxyl), 1705 (vs) with shoulder at 1725, 1265, 1240 (acetate), 743 cm.$^{-1}$ (C–Br)].

The bromohydrin was not purified because of its instability, but was oxidised directly. To a suspension in acetic acid (0·1 g. in 8 ml.) a solution of chromic oxide (0·1 g.) in water (2 ml.) was added. After 30 min. water was added and the mixture extracted with ether. The washed

[15] Cameron, Evans, Hamlet, Hunt, Jones, and Long, *J.*, 1955, 2807.

and dried extract was evaporated and the residue (85 mg.) crystallised from acetone–hexane to give the desired 9α-*bromo-compound* (59 mg.), m. p. 195—200° (decomp.), $[\alpha]_D^{22}$ +132° (Found : C, 58·4; H, 7·0. $C_{23}H_{33}O_5Br$ requires C, 58·8; H, 7·1%), $\nu_{max.}$ 3420 (hydroxyl), 1728 (acetate), 1697 (ketone), 1250 (acetate), 743 cm.$^{-1}$ (C–Br).

3β-*Acetoxy*-17α-*hydroxy*allo*pregnane*-11 : 20-*dione*.—The 9α-bromo-ketone (52 mg.) in ethyl acetate (25 ml.) was hydrogenated for 4 hr. in presence of 2% palladium–strontium carbonate (130 mg.). Removal of catalyst, evaporation of solvent, and crystallisation of the residue twice from hexane yielded 3β-acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione, m. p. 171—174° (Found : C, 70·6; H, 8·6. Calc. for $C_{23}H_{34}O_5$: C, 70·7; H, 8·8%), $\nu_{max.}$ 3440 (hydroxyl), 1730 (acetate), 1705 (ketone), 1250 cm.$^{-1}$ (acetate) {Pataki *et al.*[16] give m. p. 171—173°, $[\alpha]_D^{20}$ +8°, $\nu_{max.}$ (in $CHCl_3$) 1720 and 1700 cm.$^{-1}$ and free hydroxyl band}.

Authentic 3β : 17α-dihydroxy*allo*pregnane-11 : 20-dione, kindly made available to us by Dr. J. Elks of Glaxo Laboratories, yielded a 3-acetate, m. p. 175—176·5°, $[\alpha]_D^{22}$ +10° (Found : C, 70·8; H, 8·85%), having an infrared absorption identical with that of the material prepared as above.

11β-*Hydroxytigogenin Diacetate*.—(*a*) 11β-Hydroxytigogenin (0·3 g.) was kept overnight in a mixture of acetic anhydride (1 ml.), acetic acid (1 ml.), and toluene-*p*-sulphonic acid (50 mg.). The solution was poured into sodium hydrogen carbonate solution and extracted with ether. The washed and dried extract yielded a residue (0·25 g., 77%), m. p. 106—110°, on crystallisation from acetone. Recrystallisation gave the 3β : 11β-*diacetate*, m. p. 141—142·5°, $[\alpha]_D^{21}$ −35° (Found : C, 71·8; H, 9·5. $C_{31}H_{44}O_5$ requires C, 72·0; H, 9·4%). The infrared absorption (in Nujol) showed no hydroxyl band, but 1730 (acetate) and 1250—1240 cm.$^{-1}$ (acetate) bands were strong and the spiroketal bands were present. The same compound was obtained in lower yield by using the same reaction mixture as above, but with one drop of 60% perchloric acid instead of the toluene-*p*-sulphonic acid, or by treatment of 11β-hydroxytigogenin (300 mg.) with *iso*propenyl acetate (2 ml.) and toluene-*p*-sulphonic acid(100 mg.).

A partial hydrolysis of the diacetate (0·9 g.) was achieved by dissolving it in a mixture of chloroform (10 ml.) and methanol (3·5 ml.) and adding water (3·5 ml.) followed by concentrated hydrochloric acid (2·1 ml.), keeping the temperature +23°. After 48 hr. at 5° the product was recovered by evaporation. Purification was extremely difficult : a material which separated from light petroleum (b. p. 60—80°) was amorphous and had m. p. 202·5—205°, $[\alpha]_D^{22}$ −39°. The infrared absorption distinguished it from the diacetate or the 3-monoacetate. The (?)11β-monoacetate in Nujol showed $\nu_{max.}$ 3240 (bonded hydroxyl), with a shoulder at 3160 and acetate bands at 1732 and at 1270—1240 cm.$^{-1}$ (complex). The 3-monoacetate in Nujol has $\nu_{max.}$ 3480, 1715, and 1270 cm.$^{-1}$.

Attempts were made to hydrolyse the 11-monoacetate by 0·5N-ethanolic potassium hydroxide at room temperature or by 0·3N-sodium methoxide in boiling methanol, but without success, for the infrared absorption was unchanged. Complete hydrolysis resulted from boiling it for 1 hr. with 4% potassium hydroxide in ethanol. With 2% potassium hydroxide the starting material was recovered.

3β : 11β-*Diacetoxy*allo*pregn*-16-*en*-20-*one*.—This was obtained by oxidation of 11β-hydroxy-ψ-tigogenin triacetate, prepared by the usual method,[16] but not purified or characterised. It formed crystals from light petroleum (b. p. 60—80°), having m. p. 111° and 148—156°, $\lambda_{max.}$ 238 mμ (log ε 3·8, in EtOH) (Found : C, 73·9; H, 8·8. $C_{25}H_{36}O_5$ requires C, 72·1; H, 8·7%). Infrared absorption (in Nujol) showed no hydroxyl, but bands at 1730 (acetate), 1665 (ketone), 1590 (double bond), and 1250 cm.$^{-1}$ (broad; acetate).

11β-*Acetoxy*-16 : 17-*epoxy*-3β-*hydroxy*allo*pregnan*-20-*one* was prepared by treatment of the last-named compound with alkaline hydrogen peroxide and formed crystals [from benzene–light petroleum (b. p. 60—80°)], m. p. 176—177° (Found : C, 70·7; H, 8·5. $C_{23}H_{34}O_5$ requires C, 70·7; H, 8·8%), $\nu_{max.}$ (in Nujol) 3300 and shoulder at 2920 (hydroxyl), 1730 (acetate), 1700 (ketone), 1240 (acetate), and 856 cm.$^{-1}$ (epoxide).

National Institute for Medical Research,
The Ridgeway, Mill Hill, London, N.W.7.

[*Received, July 6th*, 1956.]

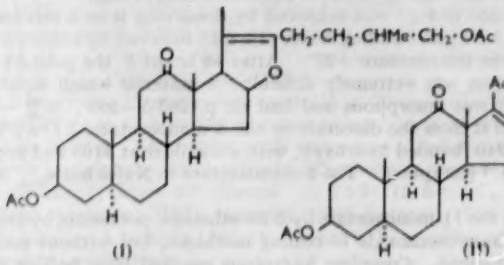
[16] Pataki, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1952, **74**, 5615.

927. *By-ways of Synthesis of Cortisone from Hecogenin. Part II.*[1] *A Route to 11-Oxygenated Compounds through 3β : 20β-Diacetoxy-11-bromoallopregnan-12-one.*

By R. K. Callow and V. H. T. James.

3β-Acetoxy*allo*pregn-16-ene-12 : 20-dione (II), obtained by degradation of ψ-hecogenin diacetate, is reduced to 3β-acetoxy*allo*pregnane-12 : 20-dione which forms a 12 : 12-ethylenedioxy-compound. Selective reduction at $C_{(20)}$ can then be carried out and 3β : 20β-diacetoxy*allo*pregnan-12-one can be monobrominated at $C_{(11)}$ and, by applying the series of reactions used previously with a 12-oxo-sapogenin, *allo*pregnane-3 : 11 : 20-trione, an intermediate in the synthesis of cortisone, is prepared.

As we explained in Part I,[1] the synthetical pathway from hecogenin to cortisone might, at least in theory, be traversed by taking the stages in different orders. In particular, the introduction of oxygen at $C_{(11)}$, previously carried out at the sapogenin stage with hecogenin, might, it was thought, be done after removal of the side chain. The diketone, 3β-acetoxy-*allo*pregn-16-ene-12 : 20-dione, obtained by degradation of ψ-hecogenin diacetate (I), or the *allo*pregnanedione derived from it, have obviously the disadvantage of possessing two activated centres. Nevertheless it was found possible to protect the 12-oxo-group as an ethylene ketal (III) and then to reduce the 20-oxo-group, thus obtaining a 12-ketone which can be brominated on $C_{(11)}$ and converted into an 11-ketone by reactions previously applied at the sapogenin stage.[2]



Several investigations were, however, necessary before this fairly direct route was completed. Initially, attempts were made to reduce selectively the 20-oxo-group in 3β-acetoxy*allo*pregn-16-ene-12 : 20-dione (II). These were unsuccessful. Hydrogenation with a palladium, platinum, or nickel catalyst in neutral solution reduced only the double bond; with a platinum catalyst in acid solution both carbonyl groups were reduced. Although zinc and acetic acid have been reported [3,4] to reduce the 20-oxo-group in similar compounds, in our experiments only the 16 : 17-double bond was reduced.

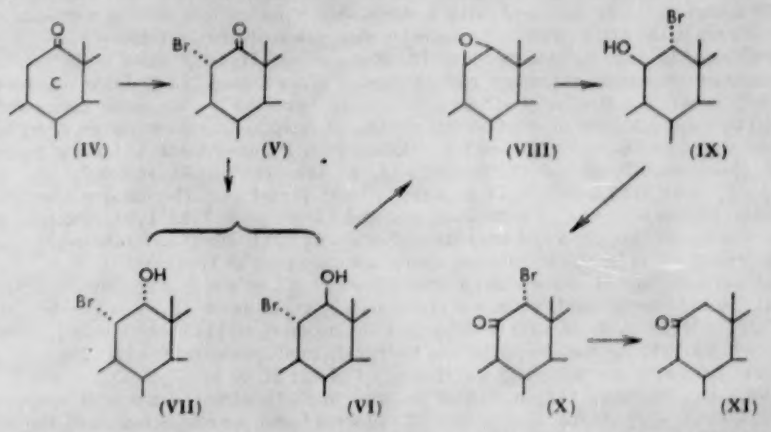
Bromination of the saturated diketone did not lead to a useful result. As much as three atomic proportions of bromine could be introduced into the molecule; one equivalent of bromine gave an approximately monobrominated product, probably not homogeneous. As on treatment with collidine this yielded mainly 3β-acetoxy*allo*pregn-16-ene-12 : 20-dione, bromination had apparently taken place predominantly at $C_{(17)}$.

These results led to an investigation of means of protecting one ketone group before bromination. 3β-Acetoxy*allo*pregnane-12 : 20-dione reacted with ethylene glycol to yield a monoketal. This could be brominated, but only with simultaneous hydrolysis of the ketal group, and the product was apparently the unpurifiable 17-bromo-derivative

[1] Part I, preceding paper.
[2] Cornforth, Osbond, and Phillipps, *J.*, 1954, 907; cf. Schmidlin and Wettstein, *Helv. Chim. Acta*, 1953, **36**, 1241.
[3] Ercoli and de Ruggieri, *Farmaco (sci.)*, 1952, **7**, 11.
[4] Nes and Mason, *J. Amer. Chem. Soc.*, 1951, **73**, 4765.

previously obtained. The ketal was at first assumed to be the 20 : 20-ethylenedioxy-compound, but it was soon clear that this was not so. Reduction by the Wolff–Kishner reaction yielded 3β-hydroxy*allo*pregnan-12-one, the constitution of which was deduced primarily from the fact that it was not identical with the known 3β-hydroxy*allo*pregnan-20-one. Reduction with lithium aluminium hydride yielded 12 : 12-ethylenedioxy*allo*-pregnane-3β : 20β-diol (for assignment of configuration at $C_{(20)}$ cf. Klyne [5]), hydrolysed to 3β : 20β-dihydroxy*allo*pregnan-12-one. In this case also the constitution was deduced from its difference from 3β : 12β-dihydroxy*allo*pregnan-20-one, which was prepared from hecogenin through the stages rockogenin, ψ-rockogenin triacetate, and 3β : 12β-diacetoxy-*allo*pregn-16-en-20-one. Positive proof of the formation of the 12-ethylene ketal from the 12 : 20-diketone is, of course, provided by the preparation of the 11-oxo-compounds described below. The observation by Adams *et al.*[6], published after the present work had been completed, that 17α-hydroxy*allo*pregnane-12 : 20-dione undergoes ethylene ketal formation exclusively at $C_{(12)}$ is in accord with our conclusion.

3β : 20β-Dihydroxy*allo*pregnan-12-one, now an accessible substance, thus provides a suitable starting point for bromination and ultimately introduction of oxygen at $C_{(11)}$. Surprisingly, the substance itself was inert towards bromine under the usual conditions. This may perhaps be due to interaction of the groups at $C_{(12)}$ and $C_{(20)}$. Infrared absorption indicates hydrogen-bonding in the diol and 3β-monoacetate but not in the diacetate. It



was found that the 3β : 20β-diacetate (IV) reacted readily with bromine to form a mono-bromo-compound, 3β : 20β-diacetoxy-11-bromo*allo*pregnan-12-one (V), which was reduced by sodium borohydride to a complex mixture, of which the 11α-bromo-12β-hydroxy- and the 11α-bromo-12α-hydroxy-compound (VI and VII) were major constituents. The former reacted with alkali to give the 11β : 12β-epoxide (VIII); the latter, under similar conditions, gave the original 12-ketone. The 11β : 12β-epoxide, or its acetate, was converted, by way of intermediates (IX and X) which were not completely characterised, into the known *allo*pregnane-3 : 11 : 20-trione (XI), an intermediate in cortisone synthesis, the series of reactions being essentially that described by Cornforth *et al.* and by Schmidlin and Wettstein for hecogenin derivatives,[2] and shown in the partial formulæ.

Connected with this work is an investigation of the possibility of introducing the 17α-hydroxy-group into 3β-hydroxy*allo*pregnane-12 : 20-dione, by the method of Julian *et al.*[7], with the sequence: 16 : 17-epoxide, 16-bromo-17α-hydroxy-compound, 17α-hydroxy-compound. In the last stage a difficulty was encountered: treatment of the bromohydrin with zinc and acetic acid yielded 3β-acetoxy*allo*pregnane-12 : 20-dione,

[5] Klyne, "Ciba Foundation Colloquia on Endocrinology," London, Churchill, 1953, Vol. 7, p. 127.
[6] Adams, Kirk, Patel, Petrow, and Stuart-Webb, *J.*, 1954, 2209, 2298.
[7] Julian, Meyer, Karpel, and Waller, *J. Amer. Chem. Soc.*, 1950, **72**, 5145.

perhaps by initial elimination of hypobromous acid to give the Δ^{16}-compound (cf. Fieser and Ettorre [8]) and reduction of the latter. The required 17α-hydroxy-20-ketone was obtained by debrominating the bromohydrin with Raney nickel in alcohol. Independently Mueller, Stobaugh, and Winniford [9] described this series of reactions but claimed to have obtained the 17α-hydroxy-compound with zinc and acetic acid. However, Dr. Mueller, in a personal communication, withdrew this claim: he had, in fact, obtained 3β-acetoxy-*allo*pregnane-12 : 20-dione. Adams *et al.*[6] obtained, as we did, the 17α-hydroxy-compound with Raney nickel and the 12 : 20-diketone with zinc. Before the work of Adams *et al.*[6] was published we had, independently, prepared, *via* the 21-bromo-derivative, 21-acetoxy-17α-hydroxy*allo*pregnane-3 : 12 : 20-trione; we wish only to place on record that our results are in complete accord with theirs.

Infrared absorption of the 12 : 20-dioxo-compounds examined showed certain anomalies in the solid state, particularly in the C=O stretching region, which tended to be more complex than was expected, an effect which may be attributed to some peculiarity of arrangement in the crystal.

Experimental

M. p.s were determined in a Kofler apparatus with polarised light, and are corrected. Optical rotations were determined in chloroform solutions of concentrations within the limits 0·5—1·0%. Infrared absorption was measured with a double-beam instrument with a rock-salt prism (Perkin-Elmer Model 21), KBr or KCl discs being used unless otherwise stated.

Reduction of 3β-*Acetoxy*allo*pregn*-16-*ene*-12 : 20-*dione*.—(*a*) Hydrogenation in the presence of 2% palladium–strontium carbonate gave 3β-acetoxy*allo*pregnane-12 : 20-dione, m. p. 197—199°, $[\alpha]_D^{21}$ +140° (cf. Mueller *et al.*[9] who give m. p. 189—190°). The same compound was obtained by using platinum in ethyl acetate or ethanol, or nickel in ethanol–ether, or by boiling an acetic acid solution with zinc powder. Boiling with 1% methanolic potassium hydroxide yielded 3β-*hydroxy*allo*pregnane*-12 : 20-*dione*, m. p. 189—195° (from acetone), $[\alpha]_D$ +165° (Found: C, 76·1; H, 9·5. $C_{21}H_{32}O_3$ requires C, 76·0; H, 9·7%). The infrared absorption in potassium chloride showed $\nu_{max.}$ 3420 (hydroxyl) and a triple peak, 1712, 1700, 1685 cm.$^{-1}$ in the C=O stretching region. A Nujol mull showed peaks at 1714, 1698, and 1682 cm.$^{-1}$ (calcium fluoride prism). A chloroformic solution showed a simple peak at 1708 cm.$^{-1}$.

(*b*) Hydrogenation of the acetoxypregnenedione (1 g.) in acetic acid (100 ml.), Adams's catalyst (50 mg.) being used, yielded a crude *acetate*, m. p. 148·5—152°, $[\alpha]_D^{21}$ −6° [infrared absorption in Nujol at about 3300 (hydroxyl), 1730 (acetate), and 1250 cm.$^{-1}$ (broad; acetate)], hydrolysed by 10% methanolic potassium hydroxide to allo*pregnane*-3β : 12ξ : 20β-*triol*, m. p. 230—234° (from ethyl acetate), $[\alpha]_D^{19}$ −2° (Found: C, 75·2; H, 10·7. $C_{21}H_{36}O_3$ requires C, 75·0; H, 10·8%), $\nu_{max.}$ (in Nujol) at approx. 3300 and a particularly intense, sharp peak at 1054 cm.$^{-1}$.

Bromination of 3β-*Acetoxy*allo*pregnane*-12 : 20-*dione*.—An ice-cold solution of the acetate (1 g.) in alcohol-free chloroform (20 ml.) was treated with bromine (0·16 ml., 1·1 equiv.) in chloroform (22 ml.). Ethanol was added and the solution kept overnight. The colourless solution was poured into water (100 ml.) containing sodium metabisulphite (0·25 g.). The chloroform layer was washed, dried, and evaporated, and the gum treated with methanol to give crystals, m. p. 167·5—171° (Found: C, 60·5; H, 8·0; Br, 17·9. $C_{23}H_{33}O_4Br$ requires C, 60·9; H, 7·3; Br, 17·7%), $\nu_{max.}$ (Nujol) 1720, 1713, and 1695 cm.$^{-1}$. A similar *product* was obtained by bromination in acetic acid solution. The product was dehydrobrominated by boiling collidine and, after purification by chromatography, rather poorly crystalline material was isolated, identified by its infrared absorption as 3β-acetoxy*allo*pregn-16-ene-12 : 20-dione. When 2·2 or 3·3 equivalents of bromine were used in the bromination another *product* was obtained, approximating to a tribromide, m. p. 195—197° (decomp.) or 198—200° (decomp.) (from alcohol), $[\alpha]_D$ −55° (Found: C, 45·6; H, 5·4; Br, 39·0. $C_{23}H_{31}O_4Br_3$ requires C, 45·2; H, 5·1; Br, 39·3%), $\nu_{max.}$ (Nujol) 1720 and 1693 cm.$^{-1}$.

12 : 12-*Ethylenedioxy*-3β-*hydroxy*allo*pregnane*-12 : 20-*dione*.—A solution was prepared by boiling under reflux with a Dean and Stark water trap, and in a current of nitrogen, a mixture of toluene (100 ml.), freshly distilled ethylene glycol (3 ml.), and toluene-*p*-sulphonic acid (50 mg.). When the condensate had become clear, 3β-acetoxy*allo*pregnane-12 : 20-dione (1·8 g.) was added

[8] Fieser and Ettorre, *J. Amer. Chem. Soc.*, 1953, **75**, 1700.
[9] Mueller, Stobaugh, and Winniford, *ibid.*, p. 4888.

and boiling continued until no more water condensed (2 hr.). The cooled solution was washed with sodium hydrogen carbonate solution and water, dried, and evaporated under reduced pressure. The residue with methanol yielded the *ketal acetate* (1·27 g.), m. p. 157—160°, rising to 161—164·5° on recrystallisation, $[\alpha]_D^{22}$ +104° (Found, after drying at 90° *in vacuo*: C, 71·7; H, 9·2. $C_{25}H_{38}O_5$ requires C, 71·7; H, 9·2%), $\nu_{max.}$ 1725 and 1700 and ($CHCl_3$) 1720 and inflexion at 1705 cm.$^{-1}$. Hydrolysis of the acetate by 5% methanolic sodium hydroxide at room temperature and crystallisation of the product from ethyl acetate–light petroleum (b. p. 60—80°) gave 12 : 12-*ethylenedioxy*-3β-*hydroxy*allo*pregnane*-12 : 20-*dione*, m. p. 198·5—200°, $[\alpha]_D^{21}$ +115° (Found: C, 73·1; H, 9·6. $C_{23}H_{36}O_4$ requires C, 73·3; H, 9·65%), $\nu_{max.}$ 1702 cm.$^{-1}$ in potassium bromide; a single peak was also observed in carbon disulphide. Resolution into two adjacent peaks was observed in a Nujol mull.

Bromination of 3β-hydroxy*allo*pregnane-12 : 20-dione and the 12-ethylene ketal was carried out under the same conditions for each substance, in ice-cold chloroform with 1·1 equiv. of bromine. The products, crystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 131—134° and 133—135°, respectively. They had identical infrared absorptions with $\nu_{max.}$ (CS_2) 1715 and 1700 cm.$^{-1}$ or (Nujol) 1695 cm.$^{-1}$. The composition approximated to that of a monobromo*allo*pregnane-12 : 20-dione (Found, for the product from the ketal: C, 58·8; H, 7·5; Br, 23·4. Calc. for $C_{21}H_{31}O_3Br$: C, 61·4; H, 7·6; Br, 19·5%).

Reduction of the 12-Ethylene Ketal or its Acetate.—(a) *Wolff–Kishner method.* The ketal (2·47 g.), treated with sodium methoxide [from sodium (3 g.) and methanol (34 ml.)] and hydrazine hydrate (95%; 3·3 ml.) at 200° for 6 hr. yielded material which was purified by adsorption from benzene solution on alumina and elution with benzene containing 10% of chloroform. The product, 3β-*hydroxy*allo*pregnan*-12-*one* (1 g.), had m. p. 197—199° (from hexane), $[\alpha]_D^{21}$ +109° (Found: C, 79·5; H, 11·1. $C_{21}H_{34}O_2$ requires C, 79·2; H, 10·8%). The infrared absorption spectrum showed bands at 3220 (hydroxyl) and 1698 (ketone) and an intense sharp peak at 1040 cm.$^{-1}$. The *acetate*, crystallised from aqueous methanol, had m. p. 138—141·5°, $[\alpha]_D^{21}$ +86° (Found: C, 76·5; H, 10·3. $C_{23}H_{36}O_3$ requires C, 76·6; H, 10·1%), $\nu_{max.}$ 1725 (acetate), 1700 (ketone), and 1247 cm.$^{-1}$ (acetate).

(b) *With lithium aluminium hydride.* A solution of 3β-acetoxy-12 : 12-ethylenedioxy*allo*pregnan-20-one (3·3 g.) in dry ether (150 ml.) was added dropwise to a suspension of lithium aluminium hydride (1 g.) in ether (150 ml.). The reaction was completed by boiling (1 hr.). After dilution with water the ethereal solution and extract were washed, dried, and evaporated. The residue (2·8 g.) yielded 12 : 12-*ethylenedioxy*allo*pregnane*-3β : 20β-*diol* in prisms (from acetone), m. p. 197—202°, $[\alpha]_D^{21}$ +48° (Found: C, 73·1; H, 10·2. $C_{23}H_{38}O_4$ requires C, 73·0; H, 10·1%). There was intense absorption in the infrared at 3400 cm.$^{-1}$ (hydroxyl), but none in the C=O stretching region. By boiling the ketal-diol with methanolic hydrochloric acid 3β : 20β-*dihydroxy*allo*pregnan*-12-*one* was obtained, m. p. 238—243°, $[\alpha]_D^{21}$ +91° (Found: C, 75·3; H, 10·2. $C_{21}H_{34}O_3$ requires C, 75·3; H, 10·3%), $\nu_{max.}$ 3440 (shoulder at 3380) (hydroxyl) and 1680 cm.$^{-1}$ (ketone). The 3β-*monoacetate*, obtained by heating with acetic anhydride for 1 hr. at 100°, had m. p. 199—207°, $[\alpha]_D^{21}$ +72°, $\nu_{max.}$ 3400 (sharp: hydroxyl), 1738 (acetate), 1685 (ketone), and 1245 cm. (acetate). When acetylation was carried out in boiling acetic anhydride for 1 hr. the product was the *diacetate*, crystals (from acetone or hexane), m. p. 141—143°, $[\alpha]_D^{21}$ +96° (Found: C, 71·4; H, 9·0. $C_{25}H_{38}O_5$ requires C, 71·7; H, 9·2%). The infrared absorption showed no hydroxyl band, but there was a broad, unresolved band, $\nu_{max.}$ at 1725 cm.$^{-1}$ in the C=O stretching region, and a band at 1245 cm.$^{-1}$ (acetate).

11α-*Bromo*-3β : 20β-*dihydroxy*allo*pregnan*-12-*one*.—The diacetate (0·75 g.) in benzene (10 ml.) was treated with bromine (1·1 equiv.) in benzene (2·5 ml.). After 15 min. the bromine was completely absorbed and a precipitate was formed which dissolved after stirring for a further 30 min. The washed, dried benzene solution was evaporated at 35° under reduced pressure. The residue gave, from hexane, 3β : 20β-*diacetoxy*-11α-*bromo*allo*pregnan*-12-*one* (0·5 g.), m. p. 161—178°, $[\alpha]_D^{21}$ +56° (Found: C, 60·3; H, 7·6; Br, 15·3. $C_{25}H_{37}O_5Br$ requires C, 60·3; H, 7·5; Br, 16·1%), $\nu_{max.}$ 1730 (acetate and, presumably, ketone) and 1250 cm.$^{-1}$ (acetate).

Reduction of 3β : 20β-*Diacetoxy*-11α-*bromo*allo*pregnan*-12-*one*.—Saturated aqueous sodium hydrogen carbonate solution (5 ml.) was added to a solution of the bromo-ketone (5·14 g.) in ethanol (175 ml.) and dioxan (20 ml.). The turbid mixture was treated with sodium borohydride (0·7 g.) and stirred for 2½ hr. at 35°, and water was then added. An ethereal extract was washed, dried, and evaporated, yielding an oily residue (5·2 g.). A portion (2·4 g.) of this, dissolved in light petroleum (b. p. 60—80°), was chromatographed on neutral alumina (75 g.); the following fractions were eluted: benzene–light petroleum (1 : 40) gave successively (*a*) 0·07 g. and (*b*) 0·42 g. The proportion of benzene was increased, finally reaching 100%, and the

eluates (*c*) 1·31 g. and (*d*) 0·07 g. were obtained. Ether–benzene (1 : 1) eluted (*e*) 0·2 g. Fraction (*a*) yielded from hexane 11β : 12β-*epoxy*allo*pregnane*-3β : 20β-*diol diacetate*, m. p. 153—155°, $[\alpha]_D^{22}$ +51° (Found : C, 72·1; H, 9·2. $C_{36}H_{56}O_6$ requires C, 71·7; H, 9·2%), $\nu_{max.}$ 1730 and 1240 (acetate), 868 cm.$^{-1}$ (epoxide), and a prominent band at 1025 cm.$^{-1}$. There was no significant absorption due to a hydroxyl group. Hydrolysis with methanolic potassium hydroxide gave 11β : 12β-*epoxy*allo*pregnane*-3β : 20β-*diol*, m. p. 216—226°, $[\alpha]_D^{22}$ +5° (Found : C, 75·6; H, 10·1. $C_{31}H_{34}O_3$ requires C, 75·4; H, 10·2%), $\nu_{max.}$ 3400 (hydroxyl), 1034 (C–O), and 860 cm.$^{-1}$ (epoxide). Fraction (*b*) yielded, from hexane, 11α-*bromo*allo*pregnane*-3β : 12β : 20β-*triol* **3** : 20-*diacetate*, m. p. 170—172·5°, $[\alpha]_D^{21}$ +10° (Found : C, 60·0; H, 7·8; Br, 16·3. $C_{35}H_{59}O_6Br$ requires C, 60·1; H, 7·9; Br, 16·0%), $\nu_{max.}$ 3540 (hydroxyl), 1730 and 1245 (acetate), 1025 cm.$^{-1}$ (C–O). When boiled with 3% methanolic potassium hydroxide this was converted into 11β : 12β-epoxy*allo*pregnane-3β : 20β-diol, identical with the compound from fraction (*d*). Fraction (*c*), crystallised from hexane, yielded 11α-*bromo*allo*pregnane*-3β : 12α : 20β-*triol* **3** : 20-*diacetate*, m. p. 160—164°, $[\alpha]_D^{21}$ +5° (Found : C, 60·15; H, 7·8; Br, 16·5. $C_{35}H_{59}O_6Br$ requires C, 60·1; H, 7·9; Br, 16·0%). The infrared absorption was similar to that of the 12β-hydroxy-compound, but the hydroxyl peak was much blunter, and there were differences in the 1100—1000 cm.$^{-1}$ range. Hydrolysis by 1% methanolic potassium hydroxide yielded 3β : 20β-dihydroxy*allo*pregnan-12-one, m. p. 238—241·5°, identical with the material already described above.

Fraction (*d*) gave, from acetone–hexane, 11β-*bromo*allo*pregnane*-3β : 12α : 20β-*triol* **3** : 20-*diacetate*, m. p. 214—221°, $[\alpha]_D^{25}$ +49°. Hydrolysis by alkali yielded the (?)11α : 12α-epoxide, m. p. 200—220°, $\nu_{max.}$ 3400 (hydroxyl) and 866 cm.$^{-1}$ (epoxide) with no absorption in the C=O stretching region; an intense sharp peak was present at 1033 cm.$^{-1}$ (C–O). Fraction (*e*) gave, from acetone–hexane, (?)11β-*bromo*allo*pregnane*-3β : 12α : 20β-*triol* 3-*acetate*, m. p. 210—217°, $[\alpha]_D^{23}$ −20° (Found : C, 60·6; H, 8·0; Br, 17·6. $C_{33}H_{57}O_4Br$ requires C, 60·3; H, 8·15; Br, 17·5%), $\nu_{max.}$ 3430, 3280 (hydroxyl), 1725, 1703 (s) (? acetate), 1270, 1255 cm.$^{-1}$ (acetate). From the fact that on hydrolysis with methanolic potassium hydroxide it gave the same (?)11α : 12α-epoxide as the diacetate from fraction (*d*) it seems likely that the compound has the constitution allotted to it, but the lævorotation is anomalous. The compounds in fractions (*d*) and (*e*) presumably arise from 11β-bromo-ketone contaminating the 11α-bromo-compound.

allo*Pregnane*-3 : 11 : 20-*trione*.—(*a*) The 11β : 12β-epoxide (70 mg.) obtained from fractions (*a*) and (*b*) by hydrolysis was shaken in chloroform (10 ml.) with 48% hydrobromic acid (0·5 ml.). After 30 min. the chloroform was washed with water and evaporated. The residue, crystallised from acetone–hexane, yielded 12α-bromo*allo*pregnane-3β : 11β : 20β-triol (68 mg.), m. p. 204—210°, $[\alpha]_D^{22}$ +17° (dioxan), $\nu_{max.}$ 3380 cm.$^{-1}$ (hydroxyl). The triol (66 mg.) in acetic acid (4 ml.) was treated with chromic oxide (0·1 g.) in water (1 ml.), the mixture was shaken well and after 1½ hr. the product was extracted into chloroform and the extract was washed, dried, and evaporated. The bromo-ketone, m. p. 176—179° (from acetone–hexane), $\nu_{max.}$ 1700 (s), was debrominated by boiling with zinc in acetic acid solution. *allo*Pregnane-3 : 11 : 20-trione, m. p. 112—118°, was isolated, identical with an authentic specimen and with the material described below.

(*b*) An alternative preparation of the triketone began with the 11β : 11β-epoxy*allo*pregnane-3β : 20β-diol diacetate from fraction (*a*) of the chromatographic separation. This material (60 mg.) in chloroform (3 ml.) was treated with 48% hydrobromic acid (0·3 ml.). After 30 min. the solution was washed free from acid and evaporated, and the 12α-bromo*allo*pregnane-3β : 11β : 20β-triol **3** : 20-diacetate crystallised from acetone–hexane.

The triol diacetate (70 mg.) in 80% acetic acid (5 ml.) was treated with chromic oxide (70 mg.). After 1½ hr. water was added and the product was isolated with chloroform. 3β : 20β-Diacetoxy-12α-bromo*allo*pregnan-11-one crytallised from acetone–hexane. Debromination by zinc dust in acetic acid yielded 3β : 20β-diacetoxy*allo*pregnan-11-one (from ether–pentane), m. p. 165—173°, $[\alpha]_D^{22}$ +34°, $\nu_{max.}$ 1730 (strong; acetate), 1705 (lower; ketone), 1245 cm.$^{-1}$ (acetate). This material was hydrolysed with 10% methanolic potassium hydroxide, and the crude product oxidised with chromic oxide in acetic acid. The final product was *allo*pregnane-3 : 11 : 20-trione (from acetone–hexane), m. p. 212—218° (Found : C, 75·9; H, 8·9. Calc. for $C_{21}H_{30}O_3$: C, 76·3; H, 9·15%). The infrared absorption, with a strong band at 1705 cm.$^{-1}$, was completely identical throughout the whole spectrum with that of an authentic specimen of the trione, m. p. 211—220° (Steiger and Reichstein [10] gave m. p. 212—216°).

Rockogenin (12β-*Hydroxytigogenin*).—Hecogenin acetate was reduced by sodium borohydride, and the product purified as the acetate which, crystallised twice from methanol

[10] Steiger and Reichstein, *Helv. Chim. Acta*, 1938, **21**, 161.

(charcoal), had m. p. 199—207°, $[\alpha]_D^{22}$ −60° (dioxan). Alkaline hydrolysis yielded rockogenin (from methanol), m. p. 195—200°, $[\alpha]_D^{22}$ −63° (dioxan) {(Hirschmann *et al.*[11] give 218·5—220·5°, $[\alpha]_D$ −64° (acetone)}.

3β : 12β-*Diacetoxy*allo*pregn*-16-*en*-20-*one* was obtained by conversion of rockogenin into ψ-rockogenin by the method of Cameron *et al.*[12], acetylation of the crude product, oxidation of the acetate with chromic acid in 90% acetic acid, hydrolysis of the "diosone," and reacetylation. The product crystallised from 50% aqueous methanol and had m. p. 140—143°, $[\alpha]_D^{22}$ +19° (Found: C, 72·0; H, 8·6. $C_{31}H_{44}O_6$ requires C, 72·0; H, 8·8%), $\nu_{max.}$ 1735 (acetate), 1680 (ketone), 1590 (double bond), 1250 cm.$^{-1}$ (acetate).

3β : 12β-*Diacetoxy*allo*pregnan*-20-*one*.—The Δ^{16}-compound was hydrogenated in ethyl acetate solution, 2% palladium–strontium carbonate being used as catalyst. The gum after purification by chromatography on alumina, was crystallised from pentane and from aqueous methanol, yielding 3β : 12β-*diacetoxy*allo*pregnan*-20-*one*, m. p. 109—113°, $[\alpha]_D^{19}$ +48° (Found: C, 71·7; H, 9·3. $C_{31}H_{46}O_6$ requires C, 71·7; H, 9·2%), $\nu_{max.}$ 1735 (strong; acetate), 1710 (lower; ketone), 1250 cm.$^{-1}$ (acetate). There were many minor, but quite distinctive, differences in the "fingerprint" region from the absorption spectrum of the isomeric 3β : 20β-diacetoxy*allo*pregnan-12-one.

National Institute for Medical Research,
The Ridgeway, London, N.W.7.

[*Received, July 6th*, 1956.]

[11] Hirschmann, Snoddy, and Wendler, *J. Amer. Chem. Soc.*, 1952, **74**, 2693.
[12] Cameron, Evans, Hamlet, Hunt, Jones, and Long, *J.*, 1955, 2807.

---

928. *The Structure and Stereochemistry of Tazettine.*

By T. Ikeda, W. I. Taylor, Y. Tsuda, S. Uyeo, and H. Yajima.

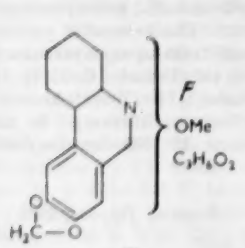
Tazettine, which is shown to contain a hemiketal moiety, can be readily transformed into the ether, deoxytazettine. A study of the Hofmann degradation of this compound showed that the true methine undergoes, in acidic media, rearrangement and loss of methanol to a compound whose structure is proved by synthesis of its degradation products, as well as by elimination to yield 6-phenylpiperonyl alcohol. The products of the Hofmann degradations of tazettine and its derivatives appear to be transformation products of the methines brought about either by the basic conditions of the reaction or by acid introduced during the isolation procedure. Acid treatment of tazettine furnishes two isomeric demethylation products, tazettinol and *iso*-tazettinol, the further study of which enables a preliminary statement to be made concerning the absolute stereochemistry of the parent base.

Tazettine, a minor alkaloid of the *Amaryllidaceae*, was first extensively investigated by Späth and Kahovec [1] who arrived at the partial structure (I) for the alkaloid. This base was later shown [2] to be identical with "base VIII" [3] and with ungernine.[4] Kondo and his co-workers [5] accumulated many valuable data which was analyzed by Wenkert,[6] who was able to deduce the structures of two of the five end products of Kondo's Hofmann degradations on tazettine which had been subject to methylation. These results along with the note by Clemo and Felton [7] could be expressed by the partial formula (II) in which the methoxy-group is placed *para* to the piperonyl residue and the presence of a readily esterifiable hydroxyl, an *N*-methyl, and an ether group had been recognized; and further the double bond was isolated. Wenkert [6] proposed a complete stereostructure for the base which, accounting satisfactorily for a few aspects of the chemistry of tazettine, most importantly could not predict or account for tazettine methine, $C_{18}H_{19}O_4N$ (Späth and

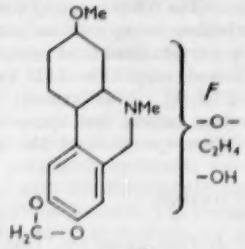
[1] Späth and Kahovec, *Ber.*, 1934, **67**, 1501.
[2] Späth, Kondo, and Kuffner, *Ber.*, 1936, **69**, 1086.
[3] Kondo, Tomimura, and Ishiwata, *J. Pharm. Soc. Japan*, 1932, **52**, 433.
[4] Norkina and Orechoff, *Ber.*, 1936, **69**, 500; Späth, Orechoff, and Kuffner, *ibid.*, p. 2446.
[5] (*a*) Kondo, Ikeda, and Okuda, *Ann. Report ITSUU Lab.*, 1950, **1**, 61; (*b*) Kondo and Ikeda, *ibid.*, 1951, **2**, 55; (*c*) Kondo, Ikeda, and Takeda, *ibid.*, p. 60; Kondo, Ikeda, and Taga, (*d*) *ibid.*, 1952, **3**, 65; (*e*) 1953, **4**, 73; (*f*) 1954, **5**, 72.
[6] Wenkert, *Experientia*, 1954, **10**, 476.
[7] Clemo and Felton, *Chem. and Ind.*, 1952, 801.

Kahovec [1]). Clemo and Hoggarth [8] confirmed this formula but, although they studied the methine in some detail, were unable to determine its structure. It remained for Taylor, Uyeo, and Yajima [9] to recognize in Späth and Clemo's results the structure (IV) for the methine which was confirmed by synthesis.

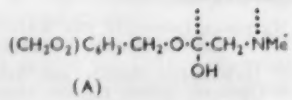
Although the methine has an ester-carbonyl group, the infrared spectrum of tazettine showed no carbonyl absorption so that the carbonyl group was masked or was being formed under Hofmann conditions. In fact, since an ester of dimethylglycine (IV) was being formed, the partial structure (A) appeared possible for tazettine in which under



(I)



(II)



(A)

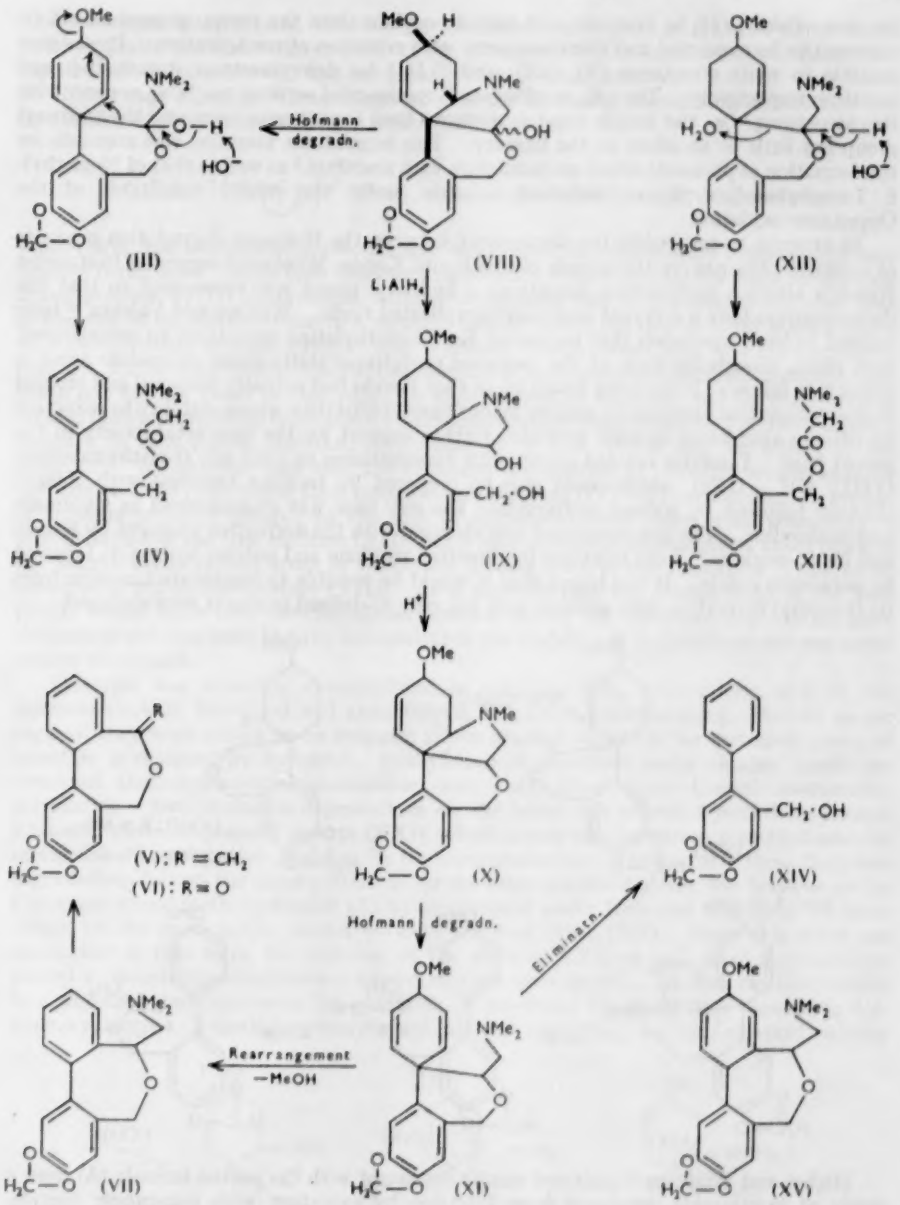
Hofmann condition the dotted bonds were broken. If the partial formula (A) were correct, tazettine might be expected to react with carbonyl reagents under a variety of conditions which it did not, as already stated by Kondo.[5a] However, with lithium aluminium hydride (contrary to Kondo's preliminary experiment [5f]) it was smoothly converted into a dihydro-compound, tazettadiol, which contained two readily acylatable hydroxyl groups and, in addition, in hot dilute acid lost the elements of water to form the ether, deoxytazettine. This behaviour has an exact parallel in the reactions of the hemiacetal moiety present in lycorenine.[10]

A study of the Hofmann degradation of deoxytazettine threw much light on the constitution of tazettine (cf. two preliminary communications [11]). It was found that in dilute aqueous acid at room temperature the methine readily rearranges with loss of the elements of methanol, to yield optically inactive deoxytazettine *neo*methine * (VII) whose structure was proved as follows. Hofmann degradation of the *neo*methine furnished trimethylamine and the nitrogen-free compound (V) which, although showing no infrared carbonyl absorption, gave, as expected, a 2 : 4-dinitrophenylhydrazone. Oxidation of this compound (V) with potassium permanganate gave the lactone (VI) from which 4 : 5-methylenedioxydiphenyl-2 : 2′-dicarboxylic acid was obtained by further oxidation. The constitutions of the last two compounds and therefore of the *neo*methine (VII) were confirmed by Ullmann syntheses. Methyl 6-bromopiperonylate and methyl *o*-iodobenzoate, heated at 230° for 3·5 hours with copper bronze, gave after fractionation of the products the dicarboxylic acid in 10% yield. Similarly, 6-bromopiperonaldehyde and methyl *o*-iodobenzoate gave methyl 6-formyl-3 : 4-methylenedioxydiphenyl-2′-carboxylate in 7% yield, converted into the lactone (VI) on reduction with sodium borohydride.

Once the structure of the *neo*methine was known, two structures for the true methine presented themselves, namely (XI) and (XV). In both cases, in agreement with ultraviolet and infrared evidence, the double bonds were not conjugated with each other or the piperonyl residue and were not contiguous to the methoxy-group. There were serious criticisms of structure (XV) which eliminate it; it would not be expected to survive the original alkaline Hofmann conditions since by loss of methanol it would aromatize to the

* Since conversion of tazettine methine into this substance is not merely isomerisation but involves elimination of CH_4O, the name "*neo*methine" is now preferred to "*iso*methine."

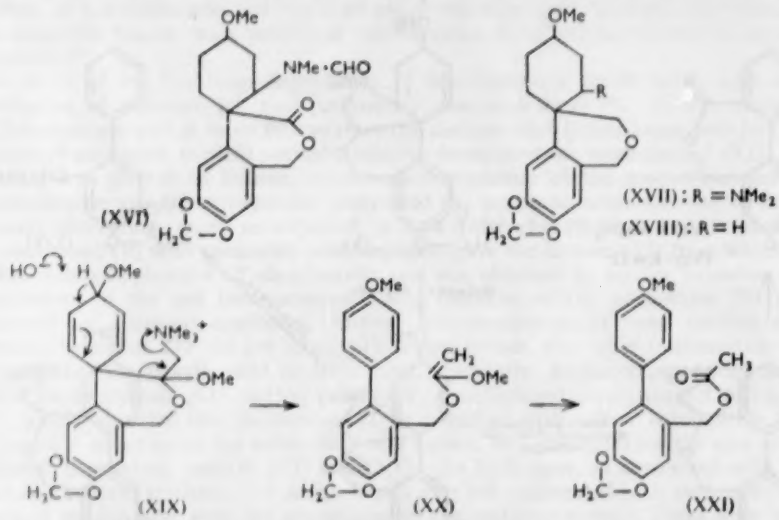
[8] Clemo and Hoggarth, *Chem. and Ind.*, 1954, 1046.
[9] Taylor, Uyeo, and Yajima, *J.*, 1954, 6183.
[10] Kitagawa, Taylor, Uyeo, and Yajima, *J.*, 1955, 1066.
[11] Ikeda, Taylor, and Uyeo, *Chem. and Ind.*, 1955, 1088; Ikeda, Taylor, Tsuda, and Uyeo, *ibid.*, 1956, 411.



*neo*methine (VII); also it cannot account for the fact that the true methine in aqueous acid gives, not only the *neo*methine, but also 6-phenylpiperonyl alcohol (XIV). Both of these facts are consistent with formula (XI) for the methine; there is no way for base-catalyzed aromatization to occur, and, with acid, rearrangement would furnish the *neo*-methine (VII) and by elimination 6-phenylpiperonyl alcohol (and probably dimethylamino-acetaldehyde but no attempt was made to isolate it). The apparent optical inactivity of

the *neo*methine (VII) is, however, not easy to explain since the rearrangement would be expected to be concerted and therefore occur with retention of configuration. It was now possible to write structures (X), (IX), and (VIII) for deoxytazettine, tazettadiol, and tazettine respectively. The pK_a results (see Experimental section) are in agreement with this structure; *i.e.*, the double bond is removed from the nitrogen atom and the hydroxyl group has little or no effect on the basicity. This formula for tazettine also accounts for the formation of phenanthridine on distillation with zinc dust,[1] as well as that of 10-methyl-6 : 7-methylenedioxyphenanthridinium chloride under the milder conditions of the Oppenauer oxidation.

In attempt to rationalize the discrepancy between the Hofmann degradation products of tazettine obtained by the schools of Späth and Kondo, Wenkert [6] suggested that under Kondo's alkaline methylating conditions a hydroxyl group was epimerized so that the decomposition took a different and more complicated route. Wiesner and Valenta [12] later seemed to have concluded that under the Kondo methylating conditions an arrangement took place, though the logic of the proposed prototropic shifts about an enolate anion is difficult to follow. It has been found by us that Kondo had actually prepared and studied *O*-methyltazettine methiodide, and we made *O*-methyltazettine whose stability to reduction by lithium aluminium hydride provided further support for the hemiketal moiety in the parent base. Tazettine reacted slowly with diazomethane to yield oily *O*-methyltazettine (VIII; OH = OMe), which could also be prepared by treating tazettine with thionyl chloride followed by sodium methoxide. The oily base was characterized as styphnate and methiodide. The last compound was identical with the derivative prepared by Kondo and his co-workers [5a] from tazettine by dimethyl sulphate and sodium hydroxide followed by potassium iodide. It was hoped that it would be possible to regenerate tazettine from its *O*-methyl derivative with aqueous acid but only ill-defined products were obtained.

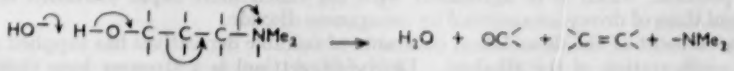


Highet and Wildman [13] obtained results consistent with the partial formula (A) from a study of tazettamide, produced from tazettine by oxidation with manganese dioxide. Further degradation of tazettamide has now provided striking confirmation of the correctness of formula (VIII) for tazettine. Dihydrotazettamide (XVI), on reduction with lithium aluminium hydride followed by digestion with dilute acid, furnished the ether (XVII) which on Emde degradation of its methochloride gave the nitrogen-free compound (XVIII).

[12] Wiesner and Valenta, British Industries Fair Review (April 1956), *Chem. and Ind.*, 1956, R 36.
[13] Highet and Wildman, *ibid.*, 1955, 1159.

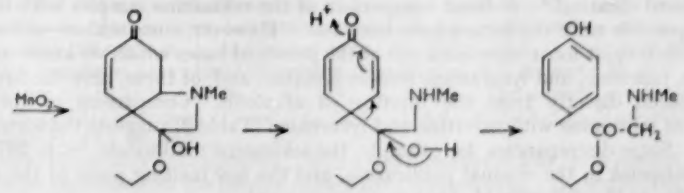
This substance, in agreement with its structure which has a plane of symmetry, was found to be optically inactive. A synthesis of the compound (XVIII) should not only confirm the structure of tazettine but also solve much of its stereochemistry.

Highet and Wildman [13] have suggested that the Hofmann degradation of tazettine and its dihydro-derivative are concerted internal eliminations :



This type of four-centre reaction would only be expected to occur readily if the centres were linearly coplanar.[14] Much later Wiesner and Valenta [12] have applied the same mechanism to our proposal (VIII) for tazettine, without recognizing that such a mechanism must lead in the case of dihydrotazettine to a methine base in which the double bond is conjugated with the piperonyl residue. Highet and Wildman [13] have shown, and we have confirmed, that the double bond in dihydrotazettine methine is not conjugated with the aromatic ring. From our results, given in this paper, it appears that in tazettine and its derivatives a normal Hofmann reaction takes place, subsequent changes being dependent on the methine's stability to base (under Hofmann conditions) or to acid (which may be added in the isolation). We consider then that the Hofmann degradation of tazettine affords initially the true methine (III) which then aromatizes to the base (IV) with concomitant formation of an ester-carbonyl group. In the case of dihydrotazettine there is no possibility of aromatization of the true methine (XII), but a rate-controlled displacement takes place at the benzyl-allylic carbon atom in which the driving force is the formation of the ester-carbonyl group in the product (XIII). It is unlikely that the double bond in the base (XIII) would move into the conjugated position during the Hofmann degradation since Weinstock and Bordwell [15] have demonstrated the stability of 3-phenyl*cyclo*hexene under similar conditions.

Tazettine was smoothly demethylated in refluxing 10% hydrochloric acid to two isomeric alcohols, tazettinol and *iso*tazettinol, the latter predominating. As the names suggest, they were shown to be epimeric allylic alcohols in which the methoxyl group of tazettine is replaced by hydroxyl. Methylation of tazettinol under alkaline conditions furnished *O*-methyltazettine methiodide, and *iso*tazettinol gave *O*-methyl*iso*tazettine methiodide. Two Hofmann degradations on the latter salt affords 2-*p*-methoxyphenyl-4 : 5-methylenedioxybenzyl acetate (XXI), which is also obtained from *O*-methyltazettine methiodide,[16] among other products, by the same procedure. The course of these Hofmann degradations follows the same pattern as for the cases discussed above, the first one giving a methine whose methohydroxide (XIX) decomposed under Hofmann conditions by base-attack on the most acidic proton to yield the enol ether (XX). Since this ether can decompose in two ways, the isolation of the acetate (XXI) as well as of 2-*p*-methoxyphenyl-4 : 5-methylenedioxybenzyl alcohol was not unexpected. Another reaction leading to a diphenyl derivative was the oxidation of tazettinol by manganese dioxide to 2-*p*-hydroxyphenyl-4 : 5-methylenedioxybenzyl alcohol according to the annexed scheme

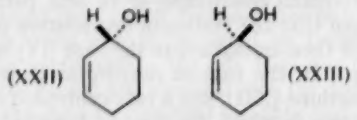


(partial formulæ) in which β-elimination and the dienone–phenol rearrangement are the two most important steps. Reduction of both tazettinol and *iso*tazettinol with lithium

[14] Cf. Barton, *J.*, 1953, 1030.
[15] Weinstock and Bordwell, *J. Amer. Chem. Soc.*, 1955, **77**, 6706.
[16] Ikeda, unpublished observations.

aluminium hydride followed by cyclization with dilute acid gave the corresponding ethers, deoxytazettinol and deoxy*iso*tazettinol. Oxidation of both of these compounds afforded the same αβ-unsaturated ketone, deoxytazettinone. Reduction of deoxytazettinone with sodium borohydride furnished deoxy*iso*tazettinol as the major product. This result implies that the hydroxyl group in the *iso*-series occupies the thermodynamically more stable position, which is in agreement with the much more rapid oxidation of deoxytazettinol than of deoxy*iso*tazettinol by manganese dioxide.

Measurement of the dissociation constants of suitable derivatives has supplied a clue as to the configuration of the alkaloid. Deoxy*iso*tazettinol is a stronger base than deoxytazettinol by 1·6 pK_a units, which suggests that the proton of conjugate acid derived from deoxy*iso*tazettinol is hydrogen-bonded to the hydroxyl group, and this requirement is met only if the groups are *cis* in ring B. It follows therefore that in tazettine the methoxyl group is *trans* to the nitrogen atom. The five-membered nitrogen-containing ring must be *cis*-fused to the *cyclo*hexene ring B because the nitrogen must be able to take up a pseudo-axial configuration which facilitates the various elimination reactions of tazettine and its derivatives involving this heteroatom. Finally Mills [17] has shown in the terpenes and steroids that the structural unit (XXII) always has a molecular rotation more positive



(XXII) (XXIII)

than its epimer (XXIII). Comparison of the epimeric allylic alcoholic derivatives derived from tazettine and the theoretical *iso*tazettine (Table 1) shows that if such considerations are valid in this substituted cyclic allylic alcohol then the configuration of the hydroxyl group in tazettine corresponds to that in (XXIII).

TABLE 1. *Optical rotations of some derivatives of tazettine.*

Normal series		*iso*-Series	
Tazettinol	+119°	*iso*Tazettinol	+261°
Deoxytazettinol	+210°	Deoxy*iso*tazettinol	+328°
Acetyldeoxytazettinol	+54°	Acetyldeoxy*iso*tazettinol	+198°
O-Methyltazettine methiodide	+66°	*O*-Methyl*iso*tazettine methiodide	+142°

The main features of the stereochemistry of tazettine have now been elucidated with the exception of the stereochemistry of the hemiketal moiety for which no evidence is yet available, and the suggested structure for further consideration is (VIII).

The opportunity is taken here to discuss the possibility that both sekisanine and sekisanoline are in reality tazettine. In 1897 Morishima [18] isolated from the bulbs of *Lycoris radiata*, together with lycorine, a second alkaloid, m. p. 200°, sekisanine (sekisan is the Chinese name for the plant). Kondo and Tomimura [19] in a re-investigation of this work found that sekisanine had m. p. 207—208°, but despite a close similarity between the physical constants of this base and " base VIII " [3] (later shown to be tazettine [2]) they were not considered identical.[3] A direct comparison of the sekisanine samples with tazettine is no longer possible since the former have been lost. However, since sekisanine was isolated without difficulty, it must have been one of the principal bases which we know today to be lycorenine, tazettine, and lycoramine besides lycorine, and, of these, only the first two can be crystallized directly from the mixture of alkaloids. Comparison of the physical constants of sekisanine with tazettine and lycorenine (Table 2) suggests the identity of the first two. Some discrepancies, for example, the sekisanine methiodide, m. p. 287°, may be due to a misprint in the original publication, and the low melting point of the acetate, is probably due to the difficulty of obtaining a pure sample.

Kondo and Tomimura [20] have also reported the isolation of an amorphous phenolic

[17] Mills, *J.*, 1952, 4976.
[18] Morishima, *Arch. Exp. Path. Pharm.*, 1897, **40**, 221.
[19] Kondo and Tomimura, *J. Pharm. Soc. Japan*, 1927, **47**, 545.
[20] Kondo and Tomimura, *ibid.*, 1928, **48**, 438.

alkaloid named sekisanoline, $C_{18}H_{23}O_5N$, from *Lycoris radiata* Herb. Repetition of this work led to the isolation of a base, m. p. 208°, from the phenolic fraction which was shown to be identical with tazettine by direct comparison. The weak acidity is probably due to the hydroxyl group since *O*-methyltazettine was found to be insoluble in alkali. That

TABLE 2.

	Sekisanine	Tazettine $C_{18}H_{21}O_5N$	Lycorenine $C_{18}H_{23}O_4N$
Analysis	C, 66·5, 66·4 H, 6·7, 5·8 N, 5·06, 4·6	65·3 6·4 4·2	68·2 7·3 4·4
M. p.	207—209°	207—209°	199—200°
$[\alpha]_D$ (EtOH)	+114·6°	+121·6°	+126·5°
Picrate, m. p.	212°	211°	Not readily cryst.
Hydrochloride, m. p.	211°	206°	,,
Methiodide, m. p.	287°	228°	260°
Acetate	72°	125°	180°
Methoxyl	None	One	One
Methylenedioxy	Present	Present	Absent
N-Methyl	Present	Present	Present

sekisanoline was impure tazettine is further supported by its empirical formula and a positive test for a methylenedioxy-group, although the reported optical rotation of sekisanoline was quite different from that of tazettine.

EXPERIMENTAL

Ultraviolet spectra were measured in ethanol.

Tazettadiol.—Lithium aluminium hydride (0·5 g.) was added portionwise with stirring to tazettine (1·5 g.) in tetrahydrofuran (50 ml). Twelve hours later, after addition of chloroform and a little water, the inorganic salts were filtered off, and the solution was dried (K_2CO_3), then evaporated to dryness. On trituration with ether the resulting oil crystallized, yielding *tazettadiol* (1·15 g.), m. p. 118—119° (after crystallization from acetone or ethanol–ether), $[\alpha]_D^{26}$ +65° (*c* 1·7 in EtOH) (Found, in a sample dried over P_2O_5 at room temperature: C, 61·6, 61·3; H, 7·1, 7·1; N, 3·9. Found, in a sample dried *in vacuo* for 5 hr.: C, 65·0; H, 6·6. $C_{18}H_{23}O_5N,H_2O$ requires C, 61·5; H, 7·2; N, 4·0. $C_{18}H_{23}O_5N$ requires C, 64·9; H, 7·0%).

Tazettadiol (0·1 g.), *p*-nitrobenzoyl chloride (0·3 g.), and dry pyridine (3 ml.) were heated on a water-bath for 20 min., the pyridine was removed *in vacuo*, and water was added to the residue. The chloroform extract was washed with 5% potassium carbonate solution, dried ($MgSO_4$), and distilled, yielding the pale yellow *di-p-nitrobenzoate* (90 mg.), m. p. 184—185° (from chloroform–ethanol) (Found: C, 60·5; H, 4·7; N, 6·6. $C_{32}H_{29}O_{11}N_3$ requires C, 60·8; H, 4·6; N, 6·7%).

Deoxytazettine.—Tazettadiol (0·25 g.) was heated on a water-bath for 1·5 hr. with 3% sulphuric acid (35 ml.). The base (0·21 g.), isolated after basification and extraction with ether, furnished *deoxytazettine*, m. p. 135—136° (from ether), $[\alpha]_D^{19}$ +225° (*c* 1·8 in EtOH) (Found: C, 68·5, 68·4; H, 6·6, 6·7; N, 4·3. $C_{18}H_{21}O_4N$ requires C, 68·6; H, 6·7; N, 4·4%).

Deoxydihydrotazettine.—Deoxytazettine (0·1 g.) in ethanol (10 ml.) was shaken with 30% palladised charcoal (0·1 g.) in an atmosphere of hydrogen for 5 hr. The crude product was chromatographed in benzene over activated alumina (2 g.). The benzene eluate gave the dihydro-compound (50 mg.), m. p. and mixed m. p. 82—84°, $[\alpha]_D^{26}$ +14·8° (*c* 0·68 in MeOH), identical with a sample of deoxydihydrotazettine (Kondo *et al.*,[8d,f]) (Found: C, 67·9; H, 7·2; N, 4·2. Calc. for $C_{18}H_{23}O_4N$: C, 68·1; H, 7·3; N, 4·4%). The *picrate*, crystallized from acetone, had m. p. 191° (decomp.) (Found: C, 52·7; H, 4·9; N, 10·2. $C_{18}H_{23}O_4N,C_6H_3O_7N_3$ requires C, 52·8; H, 4·8; N, 10·3%).

Deoxytazettine Methiodide.—Tazettadiol (1·15 g.) was refluxed for 5 hr. with methyl iodide in methanol. After concentration the residue yielded from acetone (2 ml.) the *methiodide* (0·57 g.), m. p. 231—233° (decomp.), $[\alpha]_D^{12}$ +139° (*c* 0·69 in EtOH). Re-treatment of the mother-liquors with methyl iodide and methanol in a sealed tube at 100° for 3 hr. afforded an additional quantity of the salt (0·8 g.) (Found: C, 49·8, 49·6; H, 5·1, 5·0; N, 3·1. $C_{18}H_{21}O_4N,MeI$ requires C, 49·9; H, 5·3; N, 3·1%).

Deoxytazettine (25 mg.) was refluxed for 3 hr. with methyl iodide (2 g.) in methanol (5 ml.)

to furnish a methiodide (quantitative yield), m. p. 221—223° (decomp.), identical with the sample prepared as above.

Deoxytazettine Methine.—The above methiodide (0·56 g.) in water (15 ml.) was stirred for 1 hr. with excess of freshly prepared silver oxide. The filtrate was evaporated to dryness and the residue heated at 100° for 25 min. at 2—3 mm. The product was taken up in ether, which was washed with water, then concentrated to dryness. Chromatography of the oily residue (0·36 g.) over activated alumina gave the crude *methine* (0·32 g.) from the benzene eluate; this had $[\alpha]_D^{17}$ −64·2° (*c* 1·25 in EtOH), $\lambda_{max.}$ 245 and 290 mμ (log ε 3·74 and 3·60) (Found: C, 67·7; H, 6·9. $C_{18}H_{23}O_4N$ requires C, 69·3; H, 7·0%).

The methine was converted into its *methiodide* by dissolving it (60 mg.) in methanol containing methyl iodide (3 g.) in the presence of potassium carbonate (50 mg.).

This derivative, crystallized from acetone, had m. p. 203—205° (decomp.), $[\alpha]_D^{18}$ −72·1° (*c* 0·6 in EtOH), $\lambda_{max.}$ 245 (shoulder) and 290 mμ (log ε 3·84 and 3·67) (Found: C, 51·0; H, 5·5; N, 3·0; OMe, 6·0. $C_{19}H_{23}O_4N,CH_3I$ requires C, 51·0; H, 5·6; N, 3·0; OMe, 6·6%).

Deoxytazettine neo*Methine.*—(*a*) The above methine (70 mg.) was dissolved in 5% hydrochloric acid (10 ml.); after a few minutes the clear solution became turbid and deposited crystals which were removed after 1 hr. by extraction with ether. Evaporation of the ether afforded 6-phenylpiperonyl alcohol (17 mg.), m. p. and mixed m. p. 102—104°. The aqueous acidic solution was made alkaline, then extracted with ether, to give the neo*methine* as an oil (52 mg.) which was characterized as its *methiodide*, m. p. 251° (decomp.) (from acetone), $[\alpha]_D^{18}$ ±0° (*c* 0·51 in EtOH) (Found: C, 52·1, 52·1; H, 4·8, 4·9; N, 3·7; OMe, 0·0. $C_{18}H_{19}O_3N,CH_3I$ requires C, 51·9; H, 5·1; N, 3·2%).

(*b*) Deoxytazettine methiodide (1·37 g.) in water was shaken with excess of freshly prepared silver oxide for 1 hr. After removal of the inorganic material, the filtrate and washings were evaporated to dryness *in vacuo* and heated at 100° for 30 min., then extracted with ether. Removal of the bases with 5% hydrochloric acid left 6-phenylpiperonyl alcohol as a neutral fraction (0·3 g.) which crystallized readily on concentration of the ether solution and had m. p. and mixed m. p. 101—102°. Regeneration of the basic fraction from the acidic solution gave the crude oily methine (0·55 g.) which was characterized as its methiodide (0·51 g.), m. p. 249—251° (decomp.) from acetone, identical with the *neo*methine methiodide, m. p. 251° (decomp.), described above.

2-*Methylene*-3 : 4-*benzo*-5 : 6-(3 : 4-*methylenedioxybenzo*)-*oxa*cyclo*hepta*-3 : 5-*diene* (5 : 7-*Dihydro*-7-*methylene*-2 : 3-*methylenedioxydibenz*[*c*,*e*]*oxepine*).—The above methine methiodide (0·45 g.) was converted into the hydroxide with silver oxide, then heated *in vacuo* at 100° for 15 min., after which it solidified. The ether extract, when washed with 5% hydrochloric acid, furnished the neutral optically inactive *product* (0·21 g.), m. p. 147—151° as leaflets [Found: C, 76·2, 76·0; H, 4·9, 4·6%; *M* (Rast), 250, 262. $C_{14}H_{12}O_3$ requires C, 76·2; H, 4·8%; *M*, 252] [2 : 4-*dinitrophenylhydrazone*, m. p. 227—229°, from ethanol (Found: C, 58·6; H, 4·3; N, 12·0. $C_{22}H_{16}O_7N_4$ requires C, 58·7; H, 4·0; N, 12·4%)].

The trimethylamine evolved during the degradation was collected in hydrochloric acid and precipitated as its aurichloride, m. p. and mixed m. p. 238° (decomp.) (Found: C, 9·2; H, 2·2; Au, 49·3. Calc. for $C_3H_9N,HAuCl_4$: C, 9·0; H, 2·5; Au, 49·4%).

2-*Hydroxymethyl*-4 : 5-*methylenedioxydiphenyl*-2′-*carboxylic Lactone.*—Potassium permanganate (0·4 g.) in acetone (30 ml.) was added dropwise at 50° during 6 hr. to the above methyleneoxa*cyclo*heptadiene (0·13 g.) in acetone (30 ml.). The mixture was set aside overnight and, after excess of sulphur dioxide had been bubbled in, water and 5% sulphuric acid (5 ml.) were added and the whole extracted exhaustively with ether. The extract, washed successively with 4% sodium carbonate solution and water, furnished a crystalline residue (80 mg.) which yielded the pure *lactone*, m. p. 151—152°, from acetone–methanol (Found: C, 71·3, 71·0; H, 3·9, 3·9. $C_{15}H_{10}O_4$ requires C, 70·9; H, 4·0%).

4 : 5-*Methylenedioxydiphenyl*-2 : 2′-*dicarboxylic Acid.*—(*a*) The above lactone (40 mg.) was refluxed for 1 hr. with 8% ethanolic potassium hydroxide (20 ml.), then neutralized with carbon dioxide and evaporated to dryness. To a solution of this salt mixture, potassium permanganate (0·1 g.) in water (30 ml.) was added during 5 hr. at 50°. After acidification with 20% sulphuric acid and decolorization with sulphur dioxide, the solution was extracted with ether, to give after extraction with 5% aqueous sodium carbonate the crude *diacid* (12 mg.), m. p. 251—252° after one crystallization from methanol (Found: C, 63·0; H, 3·5. $C_{15}H_{10}O_6$ requires C, 62·9; H, 3·5%).

(*b*) Methyl 6-bromopiperonylate (5 g.), methyl *o*-iodobenzoate (6 g.), and copper bronze (7 g.) were heated in a sealed tube at 225—230° for 5 hr., then cooled and taken up in chloroform.

The filtrate was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated, and the residue (8·7 g.) distilled to yield fractions: (i) not investigated (2·8 g.), b. p. 87—120°/0·3 mm.; (ii) (1·7 g.) b. p. 132—138°/0·2 mm., yielding dimethyl diphenyl-2 : 2′-dicarboxylate, m. p. 74° after three crystallizations from methanol; (iii) (2·9 g.) b. p. 170—186°/0·07 mm., which by a combination of crystallization, chromatography, and hydrolysis furnished dimethyl 4 : 5·4′ : 5′-bismethylenedioxydiphenyl-2 : 2′-dicarboxylate (0·78 g.), m. p. 155—157° (from methanol) (Found: C, 60·1; H, 3·9. Calc. for $C_{18}H_{14}O_8$: C, 60·3; H, 4·0%), and 4 : 5-methylenedioxydiphenyl-2 : 2′-dicarboxylic acid (0·55 g.), m. p. and mixed m. p. 251—252°, identical with the degradation product of tazettine above (Found: C, 62·6, 62·8; H, 3·4, 3·4%); and (iv) (0·6 g.), b. p. 190—204°/0·07 mm., which gave dimethyl 4 : 5·4′ : 5′-bismethylenedioxydiphenyl-2 : 2′-dicarboxylate (0·3 g.), m. p. 155—157° (from methanol).

Methyl 2-Formyl-4 : 5-methylenedioxydiphenyl-2′-carboxylate.—6-Bromopiperonaldehyde (2·1 g.), methyl *o*-iodobenzoate (3·5 g.), and copper bronze (4 g.) were heated in a sealed tube for 5 hr. at 230°. The resultant mixture was extracted with chloroform, the extract was filtered and evaporated; the residue, crystallized from ether, gave 2 : 2′-*diformyl*-4 : 5 : 4′ : 5′-*bismethylenedioxydiphenyl* (0·12 g.), m. p. 238—240° after many crystallizations from acetone–benzene (Found: C, 64·1; H, 3·6. $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·4%). The ethereal mother-liquor was distilled and thus afforded dimethyl diphenyl-2 : 2′-dicarboxylate (0·91 g.) (m. p. 72—74°, from methanol). The distillation residue was chromatographed in benzene over activated alumina (20 g.), and the first eluate (100 ml.) was separated by fractional crystallization in methanol into the less soluble 5-*methoxycarbonyl*-2 : 3-*methylenedioxyfluorenone* (15 mg.), m. p. 180° (Found: C, 68·0; H, 3·5. $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·6%), and the more soluble *aldehydo-ester* (0·37 g.), m. p. 103—104° (Found: C, 67·3; H, 4·2; OMe, 10·8, 11·3. $C_{14}H_{10}O_5$ requires C, 67·6; H, 4·3; OMe, 10·9%). Oxidation of the latter compound with potassium permanganate gave 4 : 5-methylenedioxydiphenyl-2 : 2′-dicarboxylic acid. The second benzene eluate (100 ml.) gave, from benzene–methanol, orange-red leaflets of 1 : 2-6 : 7-*bismethylenedioxyfluorenone* (25 mg.), m. p. 278—280° (Found: C, 66·4; H, 3·0. $C_{15}H_8O_5$ requires C, 67·2; H, 3·0), and 2 : 3-methylenedioxy-5-methoxycarbonylfluorenone.

The Synthetic Lactone.—Sodium borohydride (50 mg.) in methanol (5 ml.) was added to the aldehydo-ester (142 mg.) in methanol (10 ml.). After 1 hr., potassium hydroxide was added and the whole refluxed for a further hour. The solvent was then removed *in vacuo* and the ether extract of the residue in water furnished 2 : 2′-*bishydroxymethyl*-4 : 5-*methylenedioxydiphenyl* (15 mg.), m. p. 134—135° (from ether) (Found: C, 69·5; H, 5·3. $C_{15}H_{14}O_4$ requires C, 69·8; H, 5·5%). The aqueous solution was acidified with 20% sulphuric acid and extracted with ether which was then washed with water, dried, and evaporated to dryness. The residual oil after 0·5 hr. at 100° gave the solid lactone (103 mg.), obtained pure (65 mg.) after crystallization from acetone and then ether (m. p. and mixed m. p. 151—152° with the degradation product of tazettine described above) (Found: C, 70·5; H, 4·0. Calc. for $C_{15}H_{10}O_4$: C, 70·9; H, 4·0%). When reduction of the aldehydo-ester was carried out with excess of sodium borohydride, the main product was the diol described above.

3 : 4-*Benzo*-5 : 6-(3 : 4-*methylenedioxybenzo*)-*oxacycloheptadiene* (5 : 7-*Dihydro*-2 : 3-*methylenedioxydibenz*[c,e]*oxepine*).—The above diol (70 mg.) was refluxed in ethanol (20 ml.) containing concentrated sulphuric acid (0·6 g.) for 3 hr., then after concentration to one-third of the volume water was added and the precipitate was filtered off to furnish from acetone the pure *ether*, m. p. 138—139° (Found: C, 74·7; H, 4·9. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%).

10-*Methyl*-6 : 7-*methylenedioxyphenanthridone*.—Tazettine (0·5 g.), aluminium phenoxide (5 g.), *cyclo*hexanone (50 ml.), and xylene (50 ml.) were heated under reflux for 6 hr. After addition of ice-water, the mixture was extracted repeatedly with 10% hydrochloric acid, and the combined aqueous extracts were basified with sodium hydroxide solution, extracted with chloroform, and dried (K_2CO_3). Evaporation afforded an oil (0·17 g.), which with 5% hydrochloric acid furnished a crystalline chloride (75 mg.). On recrystallization from pyridine–ethanol this gave pure 10-*methyl*-6 : 7-*methylenedioxyphenanthridinium chloride* (30 mg.), m. p. 274 (decomp.) (Found: C, 61·3; H, 4·9; N, 4·4; NMe, 3·9. $C_{15}H_{12}O_2NCl,H_2O$ requires C, 61·7; H, 4·8; N, 4·8; NMe, 5·1%), $\lambda_{max.}$ 265 and 340 mμ (log ε 4·51 and 4·07 respectively).

The iodide was obtained by addition of sodium iodide to an aqueous solution of the chloride and had m. p. >310° (Found: C, 46·8; H, 3·6; N, 3·6. Calc. for $C_{15}H_{12}O_2NI,H_2O$: C, 47·0; H, 3·7; N, 3·7%).

The phenanthridinium chloride (30 mg.) in ethanol (25 ml.) was heated on a water-bath for 1 hr. with sodium hydroxide (0·1 g.). Removal of the ethanol *in vacuo* followed by addition of dilute hydrochloric acid gave a water-insoluble substance which was taken up in chloroform.

Evaporation of the chloroform followed by recrystallization of the residue from ethanol–benzene gave 10-methyl-6 : 7-methylenedioxyphenanthridone (18 mg.), m. p. and mixed m. p. 236—238° (Found : C, 70·92; H, 4·3; N, 5·3. Calc. for $C_{15}H_{11}O_3N$: C, 71·1; H, 4·4; N, 5·5%), $\lambda_{max.}$ 250, 270, 285, 299, 310, 325, and 340 mμ (log ε 4·50, 4·23, 4·01, 4·05, 4·05, 3·93, and 3·84 respectively).

O-*Methyltazettine.*—(*a*) Tazettine (0·3 g.) in methanol (20 ml.) was kept for 10 days at room temperature in excess of ethereal diazomethane (fresh portions being added every 3 days). The mixture was evaporated to dryness, the residue extracted with 5% hydrochloric acid was then basified, and the bases were taken up in ether. Concentration of the ethereal solution afforded crystals of unchanged tazettine (84 mg.), m. p. and mixed m. p. 208°. The mother-liquor was concentrated to dryness and chromatographed in benzene over activated alumina. The first benzene eluate afforded oily *O*-methyltazettine (0·158 g.), and the second eluate a further quantity of tazettine (36 mg.). *O*-Methyltazettine was readily soluble in organic solvents and did not crystallize even after long storage at 0°; it was, however, characterized through its crystalline *styphnate*, m. p. 198° (decomp.) from methanol (Found : C, 50·6; H, 4·3; N, 9·5; OMe, 10·5. $C_{19}H_{23}O_8N,C_6H_3O_8N_3$ requires C, 50·8; H, 4·4; N, 9·5; 2OMe, 10·5%), and gave with tazettine styphnate (m. p. 204°) a depressed mixed m. p. *ca.* 184°. A sample of *O*-methyltazettine regenerated from the styphnate had $[\alpha]_D^{26}$ +88·1° (*c* 0·8 in EtOH).

(*b*) Tazettine (0·2 g.) and thionyl chloride (7 ml.) were heated on a water-bath for 40 min., then the excess of chloride was removed *in vacuo*, and the residue refluxed for 3 hr. in sodium methoxide solution prepared from sodium (0·5 g.) in methanol (50 ml.). Water was added and the whole extracted with ether which in turn was extracted with 3% hydrochloric acid. The bases were liberated with sodium carbonate and extracted with benzene. The dried extract was chromatographed over activated alumina, and the first fraction (40 mg.) furnished on addition of ethereal styphnic acid crude *O*-methyltazettine styphnate, m. p. 188—190°. The second fraction (40 mg.) gave the pure derivative, m. p. and mixed m. p. 198° with the sample prepared as above. Succeeding fractions afforded amorphous material (100 mg.) which was not further investigated.

O-Methyltazettine with methyl iodide in methanol yielded the methiodide, m. p. 138° (decomp.) (from methanol) raised to 150—152° by drying at 110° *in vacuo* (Found : C, 47·7; H, 5·5. Calc. for $C_{19}H_{23}O_6N,CH_3I,H_2O$: C, 47·5; H, 5·6%). No m. p. depression was observed when the sample was mixed with the methiodide prepared by Kondo and Ikeda by use of dimethyl sulphate and sodium hydroxide, and then potassium iodide. The *methopicrate*, formed readily on addition of saturated aqueous picric acid to *O*-methyltazettine methiodide in hot water, had m. p. 189—190° (from methanol) (Found : C, 53·0; H, 4·7; N, 9·5; OMe, 10·9. $C_{29}H_{26}O_{14}N_4,C_6H_3O_7N_3$ requires C, 53·1; H, 4·8; N, 9·5; 2OMe, 10·5%).

O-Methyltazettine (40 mg.) and lithium aluminium hydride (70 mg.) were refluxed in tetrahydrofuran (15 ml.) for 2 hr. It was isolated unchanged, being characterized as its styphnate, m. p. and mixed m. p. 198° (decomp.).

Dihydrotazettine Methine.—Dihydrotazettine (0·5 g.) was refluxed with methyl iodide (1·5 ml.) and methanol (15 ml.) to furnish the methiodide (0·4 g.), m. p. 183° (decomp.) (from ethanol) (Found : C, 47·7; H, 5·6; N, 2·9. Calc. for $C_{18}H_{23}O_6N,CH_3I$: C, 48·0; H, 5·5; N, 3·0%). This (0·3 g.) was converted into the hydroxide with silver oxide, then heated *in vacuo* for 45 min. at 100°. The product taken up in ether was converted into the *methine picrate* (0·19 g.) which was purified by crystallization from ethanol to m. p. 129—131°, raised to 137—139° on drying *in vacuo* (Found : C, 52·4; H, 5·0; N, 9·7. $C_{19}H_{25}O_5N,C_6H_3O_7N_3$ requires C, 52·1; H, 4·9; N, 9·7%). The methine generated from its picrate is an oil, $[\alpha]_D^{26}$ +15·8° (*c* 1·2 in EtOH), $\lambda_{max.}$ 245 and 290 mμ (log ε 3·74 and 3·60 respectively).

Reduction of Dihydrotazettine Methine with Lithium Aluminium Hydride.—The methine (0·22 g.) and lithium aluminium hydride (0·2 g.) in ether (10 ml.) were refluxed for 2 hr. After addition of water and filtration, the ethereal solution was concentrated and treated with a saturated solution of picric acid. The precipitated picrate (25 mg.), m. p. 92—94° was identical with dimethylaminoethanol picrate. The neutral portion (0·15 g.) of the reduction product did not crystallize and had $\lambda_{max.}$ 240 and 290 mμ (log ε 3·64, 3·55).

Tazettamide.—Tazettine (1·3 g.) in chloroform (130 ml.) was stirred with manganese dioxide (13 g.) for 48 hr. at room temperature. Chromatography of the crude product over activated alumina gave, from the benzene fraction, tazettamide (0·45 g.), m. p. 174° (lit., 176—178°), $[\alpha]_D^{18}$ +113° (*c* 0·6 in EtOH) (lit., $[\alpha]_D^{25}$ +106° in $CHCl_3$), $\lambda_{max.}$ 240 and 293 mμ (log ε 3·57 and 3·6 respectively), ν(C=O) 1666 and 1724 cm.$^{-1}$ in Nujol mull (Found : C, 62·3; H, 5·3; N, 4·0. Calc. for $C_{18}H_{19}O_6N$: C, 62·6; H, 5·6; N, 4·1%).

Dihydrotazettamide.—Hydrogenation of tazettamide in ethanol over palladium–charcoal furnished the dihydro-compound, m. p. 157—158°, $[\alpha]_D^5$ +63° (*c* 0·6 in EtOH) (lit., m. p. 161—162°, $[\alpha]_D^{25}$ +73·3 in $CHCl_3$) (Found : C, 62·9; H, 6·1. Calc. for $C_{18}H_{21}O_6N$: C, 62·2; H, 6·1%).

Reduction of Dihydrotazettamide.—Dihydrotazettamide (0·5 g.) in tetrahydrofuran was reduced with lithium aluminium hydride (0·3 g.) at room temperature. The crude oily basic fraction was heated in 3% sulphuric acid (20 ml.) at 100° for 2 hr. Basification and extraction with ether afforded the amino-ether (315 mg.), whose *picrate* crystallized in yellow needles (from ethanol), m. p. 226—228° (decomp.) (Found : C, 52·8; H, 5·2; N, 10·1. $C_{18}H_{23}O_4N,C_6H_3O_7N_3$ requires C, 52·6; H, 5·2; N, 10·2%).

Emde Degradation of the Amino-ether.—The above amino-ether (297 mg.) with methyl iodide in boiling methanol gave the methiodide (360 mg.), $[\alpha]_D^6$ −31·2° (*c* 0·7 in EtOH), which did not crystallize. The methiodide (150 mg.) was converted into its methochloride by shaking with silver chloride, then filtered and concentrated to 4 ml. 5% Sodium amalgam (20 g.) was added and the mixture heated at 100° for 6 hr., during which an oil separated and trimethylamine was liberated. The oil was taken up into ether, washed with dilute hydrochloric acid, then water, and dried (K_2CO_3). Removal of the ether gave an oil which on chromatography over activated alumina furnished, from the benzene eluate, 4-*methoxy*cyclo*hexane*spiro-4-(6 : 7-*methylenedioxy*-iso*chroman*) (XVIII) (46 mg.), m. p. 56—58° (from ethanol), $[\alpha]_D^6$ ±0° (*c* 0·6 in EtOH) (Found : C, 70·2; H, 7·2. $C_{18}H_{20}O_4$ requires C, 69·6; H, 7·3%). Repetition of this experiment gave the same product also with zero rotation.

Action of Hydrochloric Acid on Tazettine.—Tazettine (0·5 g.) in 10% hydrochloric acid (50 ml.) was heated on a water-bath for 4 hr., then cooled, washed once with benzene, basified (K_2CO_3), and extracted thoroughly with chloroform. The dried chloroform extracts on concentration afforded a syrup (0·45 g.) which was chromatographed in benzene over activated alumina. The benzene–chloroform (1 : 1) eluate gave *isotazettinol* (0·3 g.), m. p. 204—206°, $[\alpha]_D^{20}$ +261·7° (*c* 0·5 in EtOH), after crystallization from ethanol (Found : C, 64·6, 64·3; H, 6·1, 6·2; N, 4·5; OMe, 0·0. $C_{17}H_{19}O_5N$ requires C, 64·3; H, 6·0; N, 4·4%). This compound depressed the m. p. of tazettine (207°) to 172—180°, but gave no depression on admixture with a sample of the " iso-tazettine " obtained by Kondo and Ikeda.[55] *iso*Tazettinol gave a *picrate*, m. p. 223—226° (decomp.), needles from ethanol (Found : C, 51·3; H, 4·1; N, 10·4. $C_{17}H_{19}O_5N,C_6H_3O_7N_3$ requires C, 50·6; H, 4·1; N, 10·3%).

The mother-liquor from the crystallization of *iso*tazettinol was concentrated, and the residue in ethereal solution was converted into a picrate. Fractional crystallization gave a *picrate* (20 mg.), m. p. 173—175° (decomp.) with ν(C=O) at 1750 cm.$^{-1}$ (Found : C, 52·8, 52·6; H, 3·8, 3·7; N, 10·5. $C_{17}H_{17}O_4N,C_6H_3O_7N_3$ requires C, 52·7; H, 3·8; N, 10·6%). Acetylation of *iso*tazettinol with sodium acetate and acetic anhydride gave the *diacetyl derivative*, m. p. 149—151°, $[\alpha]_D^{26}$ +198° (*c* 0·6 in EtOH) (from ethanol), ν(C=O) 1740 and 1750 cm.$^{-1}$ in Nujol mull (Found : C, 62·1; H, 5·6; N, 3·3; Ac, 21·7. $C_{21}H_{23}O_7N$ requires C, 62·8; H, 5·8; N, 3·5; 2Ac, 21·5%). Hydrolysis with 3% ethanolic potassium hydroxide regenerated *iso*tazettinol.

Further elution of the column with acetone afforded *tazettinol* (0·1 g.), m. p. 187—188°, $[\alpha]_D^{26}$ +119° (*c* 0·5 in EtOH) (from water) (Found, in a sample dried at 100° over P_2O_5 for 3 days : C, 64·3; H, 5·7%). Its picrate had m. p. 206—208° (from water) (Found : C, 49·2; H, 4·3; N, 10·2. $C_{17}H_{19}O_5N,C_6H_3O_7N_3,0{\cdot}5H_2O$ requires C, 49·7; H, 4·2; N, 10·1%), and its *diacetyl derivative* m. p. 199—200°, $[\alpha]_D^{26}$ +55° (*c* 0·4 in EtOH) (from ethanol), ν(C=O) 1760 and 1730 cm.$^{-1}$ (Nujol mull) (Found : C, 62·7; H, 5·4; N, 3·4; Ac, 20·4%). Hydrolysis with 3% ethanolic potassium hydroxide regenerated tazettinol.

Deoxyisotazettinol.—(*a*) *iso*Tazettinol (70 mg.) and lithium aluminium hydride (50 mg.) were refluxed in tetrahydrofuran (10 ml.) for 3 hr., then treated with water and filtered, and the precipitate washed with chloroform. The combined organic filtrates were concentrated to dryness, to yield an oily triol (70 mg.). This was heated on a water-bath for 1 hr. with 2·5% sulphuric acid (5 ml.), then basified and extracted with ether to furnish *deoxyisotazettinol* (40 mg.), m. p. 122—123° (from ether), $[\alpha]_D^{16}$ +328° (*c* 0·39 in EtOH) (Found : C, 67·1, 67·2; H, 6·3, 6·2. $C_{17}H_{19}O_4N$ requires C, 67·8; H, 6·4%). The picrate had m. p. 203—206° (from ethanol), and the p-*nitrobenzoate* (from methanol) had m. p. 185—186° (Found : C, 63·6; H, 4·9; N, 6·3. $C_{24}H_{22}O_7N_2$ requires C, 63·9; H, 4·9; N, 6·2%).

(*b*) Tazettadiol (0·1 g.), when heated with 10% hydrochloric acid (10 ml.) for 4 hr., basified, and extracted with ether, gave a residue (80 mg.) which on chromatography in ether over activated alumina afforded, from the first eluate, deoxy*iso*tazettinol (20 mg.), m. p. and mixed m. p. 120—121°. Further elution of the column with chloroform furnished oils which were combined and converted into a mixture of *p*-nitrobenzoates. Chromatography of these esters

gave in small yield pure deoxytazettinol *p*-nitrobenzoate (5 mg.), m. p. and mixed m. p. 171—172° which depressed greatly the m. p. of the same derivative of deoxy*iso*tazettinol.

Methylation of Tazettinol.—10% Aqueous potassium hydroxide (14 ml.) was added at a rate of 30 drops an hour to a stirred mixture of tazettinol (30 mg.) and dimethyl sulphate (2·6 g.). The mixture was then neutralized with dilute sulphuric acid and extracted with chloroform. Evaporation of the chloroform solution to dryness and re-extraction of the residue with chloroform gave *O*-methyltazettine methiodide (30 mg.), m. p. and mixed m. p. 152—154° (decomp.), $[\alpha]_D^{24}$ +66° (*c* 0·95 in EtOH) (from acetone–methanol).

Methylation of iso*Tazettinol.*—*iso*Tazettinol (0·1 g.) was methylated in a way similar to that described for tazettinol, to yield *O-methylisotazettine methiodide* (0·1 g.), $[\alpha]_D^{24}$ +143° (*c* 0·95 in EtOH) (Found: C, 49·5; H, 5·4; N, 2·9; OMe, 13·1, 12·9. $C_{20}H_{26}O_5NI$ requires C, 49·3; H, 5·4; N, 2·9; 2OMe, 12·7%). The *methopicrate* had m. p. 204—205° (from methanol) (Found: C, 53·1; H, 4·7; N, 9·9. $C_{20}H_{26}O_5N,C_6H_3O_7N_3$ requires C, 53·1; H, 4·8; N, 9·5%).

Deoxytazettinone.—(*a*) Deoxy*iso*tazettinol (0·27 g.) in dry ether (30 ml.) was stirred over manganese dioxide (3 g.) for 6 days during daylight hours. The mixture was filtered and the manganese dioxide washed well with ether. Fractional crystallization, from ethanol, of the product from the ethereal filtrate gave starting material (148 mg.) and *deoxytazettinone* (30 mg.), m. p. 174—175°, $[\alpha]_D^{16}$ +398° (*c* 0·2 in EtOH), $\lambda_{max.}$ 235 and 290 mμ (log ε 4·07 and 3·79 respectively), ν(C=O) 1680 cm.$^{-1}$ (Found: C, 68·1; H, 5·7. $C_{17}H_{17}O_4N$ requires C, 68·2; H, 5·7%).

(*b*) Deoxy*iso*tazettinol (0·1 g.) in pyridine (1 ml.) was added to a suspension of chromic oxide (0·1 g.) in pyridine (1 ml.). After 12 hr. the mixture was poured into water, then the solvent was removed *in vacuo*. The residue was extracted with 3% hydrochloric acid which, after being washed with ether, was basified with ammonia, and the bases were extracted with ether to furnish the crude ketone (55 mg.) which was obtained pure (32 mg.), m. p. and mixed m. p. 172—174°, after one crystallization from methanol.

Reduction of Deoxyisotazettinone.—The above ketone (26 mg.) in methanol (2 ml.) containing sodium borohydride (20 mg.) was set aside for 2 days. After removal of the methanol *in vacuo*, water was added and the mixture was extracted with ether, then concentrated to dryness and chromatographed over activated alumina. The light petroleum–benzene (1 : 1) eluate gave an oil (3 mg.); elution with benzene then gave deoxy*iso*tazettinol (20 mg.), m. p. and mixed m. p. 121—122°. The infrared spectrum and optical rotation of this were also identical with an authentic sample.

Deoxytazettinol.—Tazettinol (163 mg.) and lithium aluminium hydride (100 mg.) were heated in tetrahydrofuran (6 ml.) for 5 hr. under reflux. After 12 hr. a little water was added and the precipitate removed by filtration, then washed with chloroform. The combined filtrates were concentrated to dryness, then dissolved in 3% sulphuric acid (20 ml.) and heated on a water-bath for 2 hr. Basification and extraction of the acidic solution afforded an oil (130 mg.) which after chromatography in benzene over activated alumina gave *deoxytazettinol* (32 mg.), m. p. 122—123°, $[\alpha]_D^{16}$ +210° (*c* 0·34 in EtOH) (from ether–light petroleum) (Found: C, 67·6; H, 6·3; N, 4·4. $C_{17}H_{19}O_4N$ requires C, 67·8; H, 6·4; N, 4·7%). The *picrate* (from ethanol) had m. p. 225° (decomp.) (Found: C, 51·8; H, 4·0; N, 10·8. $C_{17}H_{19}O_4N,C_6H_3O_7N_3$ requires C, 52·1; H, 4·2; N, 10·6%). The p-*nitrobenzoate* had m. p. 171—172° (from ethanol) (Found: C, 63·9; H, 4·9; N, 6·3. $C_{24}H_{22}O_7N_2$ requires C, 64·0; H, 4·9; N, 6·2%). The first eluate and the mother-liquors from the crystallization of deoxytazettinol were combined and converted into a mixture of picrates which was separated into a slightly soluble and a more soluble compound. The former picrate in acetone–chloroform gave, on filtration through activated alumina, deoxytazettinol (35 mg.), and the latter picrate by the same procedure furnished deoxy*iso*tazettinol (40 mg.).

Deoxytazettinone from Deoxytazettinol.—Deoxytazettinol (20 mg.) in ether (10 mg.) was stirred with manganese dioxide (0·2 g.) at room temperature for 1 hr. After removal of the manganese dioxide and concentration to dryness, the residue was chromatographed over activated alumina to yield from the benzene eluate deoxytazettinone (17 mg.), m. p. and mixed m. p. 174—175°, $[\alpha]_D^{16}$ +395° (*c* 0·5 in EtOH) [*oxime*, m. p. 204—206° after crystallization first from ethanol and then benzene, $\lambda_{max.}$ 235 and 290 mμ (log ε 4·21 and 3·68 respectively) (Found: N, 9·0. $C_{17}H_{18}O_4N_2$ requires N, 8·9%)].

6-p-*Methoxyphenylpiperonyl Alcohol from Tazettinol.*—Tazettinol (0·2 g.) and manganese dioxide (2 g.) in chloroform (20 ml.) were shaken at room temperature for 2 hr., then filtered. The filtrate was evaporated to dryness to afford a residue (54 mg.). The manganese dioxide was dissolved in aqueous sulphurous acid which was then basified with potassium carbonate and

extracted with chloroform. This solution yielded a further oxidation product (133 mg.) which was combined with the 54 mg. isolated as above and taken up again in chloroform and extracted with dilute acid which removed some unchanged starting material (20 mg.). Concentration of the chloroform solution afforded a 6-p-*hydroxyphenylpiperonyl alcohol* (32 mg.), m. p. 186—188°, $\lambda_{max.}$ 230, 257, and 292 mμ (log ε 4·16, 4·01, and 3·80 respectively) (Found: C, 69·1; H, 5·1. $C_{14}H_{12}O_4$ requires C, 68·8; H, 5·0%). Treatment of the phenol (12 mg.) with excess of diazomethane furnished 6-*p*-methoxyphenylpiperonyl alcohol, m. p. and mixed m. p. 147—149°.

Hofmann Degradation of O-*Methylisotazettine Methiodide.*—The methiodide (0·62 g.) in water (10 ml.) was shaken with excess of silver oxide, then filtered and evaporated to dryness. The residue was heated *in vacuo* at 100° for 30 min., then taken up in ether which was extracted with 3% sulphuric acid. From the ether layer 6-phenylpiperonyl alcohol (28 mg.), m. p. 102—104°, was obtained. The crude methine base (0·32 g.) isolated from the acidic solution was refluxed with methyl iodide (3 g.) in methanol (3 ml.). The crude gummy methiodide was converted into the hydroxide by means of silver oxide, and the resulting solution concentrated and heated at 100° *in vacuo* for 30 min. The product was taken up in ether, washed with 3% sulphuric acid and water, then dried and concentrated to dryness, and the residue (65 mg.) chromatographed over activated alumina. The benzene eluate afforded 6-*p*-methoxyphenylpiperonyl acetate (10 mg.), m. p. 86—88° after crystallization from light petroleum; and from the benzene methanol eluate 6-*p*-methoxyphenylpiperonyl alcohol (30 mg.), m. p. 145—147°, was obtained. Both compounds were identical with authentic samples.

Dissociation Constants.—pK_a's were found for the following compounds measured in 80% Methylcellosolve–water and in parentheses in 40% methanol–water: tazettine, 6·14 (6·86); dihydrotazettine, 6·10; tazettadiol, 6·23; *iso*tazettinol, (7·75); diacetyl*iso*tazettinol, (6·53); acetyltazettine, (5·92); deoxy*iso*tazettinol, (8·7); deoxytazettinol, (7·1).

We are indebted to Professor H. Kondo for his continued interest and to Mr. M. Fukuda for the microanalyses, M. T. Takashima for the ultraviolet spectra, and Mr. S. Oseko and Mr. Y. Matsui for the infrared spectra. We thank Mr. L. Dorfman and Dr. M. J. Allen of CIBA Pharmaceutical Products for the measurements of some infrared spectra and potentiometric titrations respectively.

School of Pharmacy, University of Osaka, Japan.
University of New Brunswick, Canada.
[Present address of W. I. T.:
CIBA Pharmaceutical Products Inc.,
Summit, New Jersey, U.S.A.]

[*Received, June 4th,* 1956.]

---

929. *Researches on Acetylenic Compounds. Part LIII.* The Relative Strengths of Some Unsaturated Carboxylic Acids.*

By G. H. Mansfield and M. C. Whiting.

Values for the dissociation constants at 25° in aqueous 0·1M-sodium chloride solution are reported for a number of acetylenic, allenic, and conjugated dienoic acids. The results permit some generalisations regarding the electronic influences of these unsaturated systems.

It has been known for some time that αβ-acetylenic acids (I) are more acidic than their ethylenic and saturated analogues, and that the acetylenic bond exerts, generally, a powerful electron-attracting influence.[1]

R·C≡C·CO_2H (I) R·C≡C·CH_2·CO_2H (II) H·C≡C·[CH_2]$_n$·CO_2H (III)

Variations already reported in the dissociation constants of acids (I) are considerable; where R = H,[2] Me,[3] Bu^n,[4] and Ph,[2] pK_a values of 1·85, 2·61, 2·85, and 2·33 have been

* Part LII, *J.*, 1956, 4073.

[1] Dippy, *Chem. Rev.*, 1939, **25**, 179; Walsh, *Trans. Faraday Soc.*, 1947, **2**, 18; Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 70.
[2] Wilson and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 1266.
[3] Jeffery, German, and Vogel, *J.*, 1937, 1604.
[4] Braude and Jones, *J.*, 1946, 128.

published. It appeared that a much wider range of data, obtained under comparable conditions, might throw light on the relative magnitude of conjugative, hyperconjugative, and inductive effects in these systems. We now report results, obtained potentiometrically at 25° in 0·10M-sodium chloride solution, for a group of acetylenic acids of the types (I—III), and for some other unsaturated acids; with a few exceptions the pK_a values are believed to be accurate to ±0·05.

Several of the acids were obtained by a modification of published procedures, an acetylenic hydrocarbon being prepared by dehydrohalogenation with sodamide in liquid ammonia and converted *in situ* into its sodium derivative, which was then treated with carbon dioxide in ethereal suspension. Although yields were sometimes inferior to those obtained by a two-stage process, the method is convenient for the preparation of small

Dissociation constants of αβ-acetylenic acids (I).

R	pK_a	Lit. value	R	pK_a	Lit. value
H	1·84, 1·84	1·85 [a]	C≡CMe	1·94, 1·94	—
Me	2·60, 2·58	2·61 [b]	C≡CEt [g]	1·89, 1·91	—
Et [d]	2·61, 2·60	—	C≡CBu^n [g]	1·89, 1·89	—
Bu^n [e]	2·59, 2·61	2·85 [c]	[C≡C]$_2$·Et [g]	1·67 [h]	—
Bu^t [f]	2·66, 2·65	—	CH:CHMe [b]	2·66, 2·67	—
CH_2·CMe_3 [f]	2·52, 2·54	—	Ph [i]	2·23, 2·23	2·23 [a]

Dissociation constants of βγ-acetylenic acids (II).

R	H [j]	Me [k]	C≡CMe [g]	CH:CH_2 [f]	Ph [f]
pK_a	3·31, 3·33	3·60, 3·58	3·23, 3·23	3·37, 3·41	3·44, 3·43

Dissociation constants of ω-acetylenic acids (III).

n	2 [l]	3 [l]	4 [l]
pK_a	4·20, 4·21	4·59, 4·60	4·57, 4·58

Dissociation constants of various acids.

Acid	pK_a	Acid	pK_a
H_2C:C:CH·CO_2H [j]	3·69, 3·68	Me·C≡C·CH:CH·CO_2H [k]	4·20 [m]
Ph·CH:C:CH·CO_2H [f]	3·68 [m], 3·71 [m]	Me·CH:CH·CH:CH·CO_2H	4·48 [m], 4·53 [m]
HC≡C·CH:CH·CO_2H [m]	3·74, 3·76	Me·CH:CH·CH:CH·CO_2H [k]	4·51 [m], 4·48 [m]

[a] Ref. 2. [b] Ref. 3. [c] Ref. 4. [d] Zoss and Hennion, *J. Amer. Chem. Soc.*, 1941, **63**, 1151. [e] Haynes and Jones, *J.*, 1946, 504. [f] This paper. [g] Jones, Thompson, and Whiting, unpublished work. [h] Ref. 17. [i] Gilman and Young, *J. Org. Chem.*, 1936, **1**, 315. [j] Ref. 6. [k] Jones, Whitham, and Whiting, *J.*, 1954, 3201. [l] Eglinton and Whiting, *J.*, 1953, 3052. [m] Ref. 5.

N.B. References are to the actual method of preparation used, rather than to the first synthesis.

quantities. 4-Phenylbut-3-ynoic and hex-5-en-3-ynoic acid were prepared by condensation of the bromomagnesium derivatives of phenylacetylene and vinylacetylene, respectively, with ethylene oxide, and oxidation of the resultant primary alcohols with chromic acid.[5]

When 4-phenylbut-3-ynoic acid was heated to 40° with 18% potassium carbonate solution, the corresponding allenic acid could be isolated in 52% yield. The ultraviolet spectra of solutions of 4-phenylbuta-2 : 3-dienoic and of 4-phenylbut-3-ynoic acids, in potassium carbonate solution after equilibration at 40°, were virtually identical, and corresponded to a 3 : 2-concentration-ratio of the two anions. This contrasts with the virtually complete conversion of but-3-ynoic into buta-2 : 3-dienoic anions under similar conditions.[6] Under more drastic conditions 4-phenylbuta-2 : 3-dienoic acid underwent hydration and fission to benzyl methyl ketone, rather than rearrangement to the αβ-acetylenic acid.[6] 4-Phenylbuta-2 : 3-dienoic acid was first obtained by the action of nickel carbonyl on 3-chloro-3-phenylprop-1-yne,[7] and its spectrographic properties will be discussed later.

[5] Heilbron, Jones, and Sondheimer, *J.*, 1947, 1589.
[6] Eglinton, Jones, Mansfield, and Whiting, *J.*, 1954, 3197.
[7] Jones, Whitham, and Whiting, *J.*, to be published.

Discussion

In the simple αβ-acetylenic acids (I), the unique position of propiolic acid (I; R = H) is at once obvious. Replacement of the terminal hydrogen atom by any alkyl group, a phenyl or a propenyl group, increases the pK_a value by 0·6—0·9.[1] The small differences among the various alkyl substituents indicate that C–H hyperconjugation is not of predominant importance in reducing the dissociation constant; the slightly increasing effect from methyl to *tert.*-butyl is reminiscent of the trend of dipole moments of the alkyl cyanides, reported by Ingold.[8] A second acetylenic bond, on the other hand, increases the dissociation constant fivefold relative to the corresponding monoacetylenic acid, but the effect of further increase in the polyacetylenic chain is much smaller.

When a methylene group is interposed between the acetylenic linkage and the carboxyl group, the effects observed when R is varied in the structure (II) are analogous, but all ΔpK_a values are smaller by a factor of 2—2·5, as is usual when a methylene group is inserted (cf. the chloro- and iodo-acids, $X\cdot[CH_2]_n\cdot CO_2H$).[9] Increasing the separation of the ethynyl and carboxyl groups produces the expected progressive weakening as n increases from 0 to 3, but hept-6-ynoic acid (III; $n = 4$) is unexpectedly strong. Conceivably this may be due to some weak cyclic interaction between the triple bond and the $\cdot CO_2^-$ grouping. The results imply that the ethynyl group approximates in electron-attracting power to an iodine atom.

In contrast to the acetylenic acids, the two stereoisomeric hexadienoic acids show almost identical dissociation constants differing little from those of monoethylenic and saturated acids. The absence of an increase in dissociation constant on passing from the 2-*trans* to the 2-*cis* isomer suggests that there is little hindrance to coplanarity in the latter. This contrasts with the cases of *o*- and *p*-toluic acid and of tiglic and angelic acid, where steric hindrance in one isomer, by inhibiting the acid-weakening effect of conjugative interaction, enables the intrinsic electron-attracting tendencies of unsaturated systems to assert themselves.[10]

Evidently the allene grouping shows net electron-attracting powers intermediate between those of ethylenic and acetylenic linkages.

Diagnostic use has already been made of the results recorded above.[11]

Experimental

The acids were dissolved in 0·10M-sodium chloride solution, 20 c.c. of a 0·01M-solution being employed when the solubility and the quantity of material permitted. In the titrations 0·1M-sodium hydroxide solution was added from a burette which could be read to 0·01 c.c., pH values being measured with a glass electrode, calomel electrode directly immersed, and a Cambridge pH meter, calibrated before and after with 0·05M-potassium hydrogen phthalate solution. The temperature was maintained at 25° ± 0·5°. Readings from the first and the last quarter of the titration were ignored; 10—15 values of the pK_a were calculated from the central portion of the titration, and the mean was determined. The standard deviation from the mean value was about 0·03, but accuracy greater than ±0·05 unit is not claimed because of systematic errors. The conditions used maintained constant ionic strength; no activity corrections were made. Each determination was carried out in duplicate when possible.

Because of shortage of material or low solubility it was necessary to work in more dilute solution, down to 0·005M, in some cases which are marked with an asterisk in the Table. Here precision was lower, and results should be taken as ±0·10 unit. Occasionally a systematic drift to lower acidity was evident as the titration proceeded, remedied by further purification of the acid involved.

4 : 4-*Dimethylpent-2-ynoic Acid.*—3 : 3-Dichloro-2 : 2-dimethylbutane[12] (31·0 g.) in ether (100 c.c.) was added to a suspension of sodamide, prepared from sodium (15 g.) in liquid ammonia (1 l.), during 40 min., and the mixture stirred for 4 hr. Ether (250 c.c.) was then added, and the

[8] Ingold, *op. cit.*, pp. 100 and 115.
[9] Derick, *J. Amer. Chem. Soc.*, 1911, **33**, 1152.
[10] Ingold, *op. cit.*, p. 744.
[11] Bullock, Jones, Mansfield, Thompson, and Whiting, *Chem. and Ind.*, 1954, 990.
[12] Favorski, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 425.

mixture transferred from the vacuum flask to a beaker; most of the ammonia evaporated during 12 hr. A further 250 c.c. of ether were added, and the mixture was warmed to 30° in a slow stream of dry nitrogen to remove the remainder of the ammonia; then a large excess of solid carbon dioxide was added. After 14 hr. water (25 c.c.) was added cautiously, followed by dilute sulphuric acid. Isolation of the acidic fraction and distillation gave the acetylenic acid (8·3 g., 33%), m. p. 48—49° (uncorr.) [Moureu and Delange [13] give b. p. 110°/10 mm., m. p. 47—48° (uncorr.)]. Its infrared spectrum showed a strong band at 2222 cm.$^{-1}$, and the equivalent weight found agreed with the theoretical value.

5 : 5-Dimethylhex-2-ynoic Acid (with J. L. H. Allan).—1 : 2-Dibromo-4 : 4-dimethylpentane [14] (40 g.) in ether (100 c.c.) was added to a suspension of sodamide, prepared from sodium (14 g.) in liquid ammonia (500 c.c.), during 90 min. After 16 hours' stirring 250 c.c. of ether were added and the mixture was heated in a stream of nitrogen for 4 hr. Ether (500 c.c.) was added, the mixture was cooled externally to −60°, and roughly powdered solid carbon dioxide was added until the 3 l.-flask was full. After 3 days dilute sulphuric acid was added, and the acidic fraction was isolated with ether, giving a residue (9·0 g.) which was sublimed at up to 120° (bath temp.)/10^{-4} mm., yielding 7·7 g. (37%) of material, m. p. 42—46°, raised with some difficulty to 46·5° by crystallisation from light petroleum at −6° (Favorski and Opel [15] give m. p. 48—49·5°).

Hexa-2 : 4-diynoic Acid.—1 : 4-Dichlorobut-2-yne [16] (61 g.) was added to a suspension of sodamide, prepared from sodium (38 g.) in liquid ammonia (500 c.c.). After 5 min. methyl iodide (71 g.) was added dropwise. After a further 2 hr., a suspension of sodamide, prepared from sodium (3 g.) in liquid ammonia (500 c.c.) was added. The mixture was stirred for 1½ hr., ether (250 c.c.) was added, and the mixture was set aside in a beaker while most of the ammonia evaporated, during 12 hr., then transferred to an autoclave containing an excess of crushed carbon dioxide. After 48 hr. the complex was decomposed with dilute sulphuric acid, and the diacetylenic acid (2·65 g., 5%) was isolated; it had m. p. 118° (Allan *et al.*[17] give m. p. 118°).

Hex-5-en-3-ynoic Acid.—A solution of chromic acid (25·5 c.c.; 6N in 12N-sulphuric acid) was added dropwise to a solution of hex-5-en-3-yn-1-ol [18] (3·4 g.) in acetone (100 c.c.), the temperature being kept near 20°. After 17 hr. water was added and the acidic fraction was isolated giving *hex-5-en-3-ynoic acid* (750 mg., 19%), m. p. 60—61° (Found: C, 65·45; H, 5·6. $C_6H_6O_2$ requires C, 65·45; H, 5·5%). Light absorption in 95% ethanol: maximum, 2230 Å, inflexion, 2320 Å; ε = 12,200 and 10,400, respectively.

4-Phenylbut-3-ynoic Acid.—4-Phenylbut-3-yn-1-ol [19] (8·0 g.) was dissolved in acetone (200 c.c.) and treated at 15—20° with a solution of chromic acid (36 c.c.; as above). After 3 hr. water was added and the acidic product isolated. Crystallisation from light petroleum gave the *acid* (4·1 g., 47%), m. p. 71° (Found: C, 75·1; H, 5·2. $C_{10}H_8O_2$ requires C, 75·0; H, 5·05%).

4-Phenylbuta-2 : 3-dienoic Acid.—The above acid (11·0 g.) was heated at 40° with potassium carbonate solution (100 c.c.; 18%) for 1 hr. Isolation of the acidic material and crystallisation from light petroleum gave the allenic acid (0·5 g.), m. p., and mixed m. p. with an authentic [7] specimen, 92° (Found: C, 75·25; H, 5·3. $C_{10}H_8O_2$ requires C, 75·0; H, 5·05%). When heated with potassium hydroxide solution (75 c.c.; 9%) at 90° for 2 hr., 4-phenylbut-3-ynoic acid (0·5 g.) gave benzyl methyl ketone (0·25 g., 60%), b. p. 106° (bath temp.)/9 mm., n_D^{19} 1·5160 (Danilov and Venus-Danilova [19] give b. p. 100—101°/14 mm., n_D^{20} 1·5168). The 2 : 4-dinitrophenylhydrazone had m. p. 155—156°, undepressed with an authentic specimen.

The authors thank the Department of Scientific and Industrial Research for a Maintenance Grant for one of them.

The University, Manchester 13.
The Dyson Perrins Laboratory, Oxford University. [*Received, June 22nd*, 1956.]

[13] Moureu and Delange, *Bull. Soc. chim. France*, 1903, **29**, 648.
[14] Whitmore and Homeyer, *J. Amer. Chem. Soc.*, 1933, **55**, 4555.
[15] Favorski and Opel, *J. Russ. Phys. Chem. Soc.*, 1918, **50**, 74.
[16] Nazarov and Elizarova, *Bull. acad. Sci. U.R.S.S.*, 1940, 189.
[17] Allan, Jones, and Whiting, *J.*, 1955, 1862.
[18] Murray and Cleveland, *J. Amer. Chem. Soc.*, 1938, **60**, 2664.
[19] Danilov and Venus-Danilova, *Ber.*, 1927, **60**, 1067.

930. *Researches on Acetylenic Compounds. Part LIV.* The Preparation and Synthetical Applications of Ethynylmagnesium Bromide.*

By E. R. H. Jones, L. Skatteböl, and M. C. Whiting.

Ethynylmagnesium bromide can be prepared in tetrahydrofuran solution by a reverse-addition technique. It converts many carbonyl compounds into the corresponding ethynylcarbinols in high yields.

In the condensation of metallic derivatives of monosubstituted acetylenes, R·C≡C·M, with carbonyl compounds, the bromomagnesium derivatives have important advantages over the sodium and lithium derivatives, and are generally chosen when possible.[1] In particular, they can readily be prepared in an organic solvent, and react smoothly with carbonyl compounds which are unstable under basic conditions. The bisbromomagnesium derivative of acetylene itself has frequently been used in this way, but although early workers probably did obtain reagents containing a certain amount of the monobromomagnesium derivative, the bisbromomagnesium compound always was clearly the major component.[1] A definite claim to have prepared the mono-compound was made by Grignard, Lapayre, and Tchéoufaki,[2] whose method involved saturation of an ethereal solution of ethylmagnesium bromide containing benzene with acetylene at 1·5 atmospheres. We must point out in this connection (*a*) that this increase in pressure could not be expected to change the course of the reaction significantly, and it has been repeatedly observed [1] that at atmospheric pressure even prolonged passage of acetylene does not alter the insoluble bis-derivative; (*b*) that we have been unable to reproduce the results described; and (*c*) that of the alleged reaction products obtained in this way, although all the known compounds, R·C≡CH, described agreed well with literature reports, that which at the time was not known (pent-1-en-4-yne) has been proved subsequently [3] to possess properties (density and refractive index) widely different from those listed. In our hands ethynylmagnesium bromide disproportionated to acetylene and the bis-derivative under conditions much milder than those specified for the condensation reactions with benzyl and alkyl bromides, etc. The reaction with benzyl bromide was said [2] to give as one product a hydrocarbon, m. p. 80°, described as dibenzylacetylene, and subsequently said to be obtained [4] by catalytic reduction of diphenyldiacetylene. Dupont, Dulou, and Lefebvre [5] have prepared dibenzylacetylene by two unambiguous routes, and find it to be a liquid at room temperature. Repeating the work of Grignard, Lapayre, and Tchéoufaki [2] they obtained 1 : 4-dibenzylbenzene, m. p. 81—83°, and suggested that it was this substance that the latter authors had isolated. It would, of course, be impossible to obtain this compound by the second method described by Grignard and Tchéoufaki.[4]

In view of recent unfavourable comments [6] on the syntheses reported by Grignard and Tchéoufaki [7] of iodotriacetylene and phenyltriacetylene, which we endorse, it appears that the claims made in these papers should be treated with great caution.

It is clear that acetylene must give ethynylmagnesium bromide as the first product of its reaction with ethylmagnesium bromide—indeed this has been proved kinetically.[8] When the gas is passed into an ether or benzene solution, however, the sparingly soluble bisbromomagnesium derivative soon separates, and does not redissolve; presumably reaction (2) proceeds with a rate comparable with that of reaction (1), and, because the ethylmagnesium bromide is in excess, the bismagnesium bromide is formed almost quantitatively. Since the reactions of acetylenes with Grignard reagents in non-polar solvents are not

* Part LIII, preceding paper.

[1] For a general review see Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworth London, 1955, pp. 13 and 16, and references cited there.
[2] Grignard, Lapayre, and Tchéoufaki, *Compt. rend.*, 1928, **187**, 517.
[3] Paul and Tchelitsheff, *ibid.*, 1951, **233**, 1116.
[4] Grignard and Tchéoufaki, *ibid.*, 1929, **188**, 1531.
[5] Dupont, Dulou, and Lefebvre, *Bull. Soc. chim. France*, 1954, 653.
[6] Schlubach and Franzen, *Annalen*, 1951, **573**, 115.
[7] Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 351.
[8] Kleinfeller and Lohmann, *Ber.*, 1938, **71**, 2608.

instantaneous and do not involve free ions—unlike analogous reactions with sodamide in liquid ammonia, for example [9]—one cannot assume either that equilibrium (3) would favour ethynylmagnesium bromide, or that it would be attained at a practicable rate. In fact, no clear-cut exchange reaction such as (3), between one acetylene and the bromomagnesium derivative of another, has yet been demonstrated; and even the reactions with alkylmagnesium halides are quite slow.[10] The best hope of obtaining ethynylmagnesium bromide therefore lay in avoiding reaction (2) by maintaining a local excess of acetylene through an inverse-addition technique, while at the same time further attempting to minimise the disproportionation reaction (3) by employing a good solvent for acetylene and for the bis-bromomagnesium derivative, such as tetrahydrofuran.

$$\text{(1)}\quad HC{\equiv}CH + EtMgBr \longrightarrow HC{\equiv}C{\cdot}MgBr + EtH$$

$$\text{(2)}\quad HC{\equiv}C{\cdot}MgBr + EtMgBr \longrightarrow BrMg{\cdot}C{\equiv}C{\cdot}MgBr + EtH$$

$$\text{(3)}\quad HC{\equiv}CH + BrMg{\cdot}C{-}C{\cdot}MgBr \rightleftharpoons 2HC{\equiv}C{\cdot}MgBr$$

When these conditions were employed a reagent was obtained which converted carbonyl compounds into their ethynylcarbinols in yields of up to 85%, no detectable quantities of the glycols being isolated. When the solution of the reagent was cooled a solid separated which was analysed by decomposition with an excess of dilute sulphuric acid, measurement of the volume of acetylene produced, and back-titration to estimate magnesium (as BrMg·OH). Values of 0·96 and 0·90 were obtained in replicate experiments for the ratio [C_2H_2 liberated] : [acid consumed]. When the solution was evaporated below 20° at 0·1 mm., partial disproportionation (—3) occurred, and decomposition of the residue gave an acetylene : magnesium ratio of 0·79, 0·74, and 0·74; warming to 50° *in vacuo* reduced the ratio to 0·37. With the normal procedure, when the acetylene was passed into the ethylmagnesium bromide, and even though the gas-stream was continued for some time beyond apparent saturation, the sparingly soluble derivative which separated gave ratios of acetylene : magnesium of 0·37 and 0·40 on decomposition. Thus the inverse-addition technique is essential for success. More surprisingly, the use of pure tetrahydrofuran as solvent is also an important factor; one experiment in which a 1 : 1 mixture of ether and

Reactions of ethynylmagnesium bromide.

Reagent	Product	Yield (%)	Yield (%) by other methods
Me·CO·Et	MeEtC(OH)·C≡CH	70	78 [a]
Me·CO·CH_2Cl	Me·C(OH)(CH_2Cl)·C≡CH	60	25 [b]
Me·COPh	MePh(OH)·C≡CH	35	47 [c]
Ph_2CH·CHO	Ph_2CH·CH(OH)·C≡CH	75	—
CH_2=CH·CHO	H_2C=CH·CH(OH)·C≡CH	45	58 [d]
CH_2·CH=CH·CHO	CH_2·CH=CH·CH(OH)·C≡CH	85	75 [e]
Ph·CH=CH·CHO	Ph·CH=CH·CH(OH)·C≡CH	60	2,[f] 13·5 [g]
Bu·C≡C·CHO	Bu·C≡C·CH(OH)·C≡CH	85	—
H·CO_2Et	HC≡C·CH(OH)·C≡CH	40	<1 [h]
Cl·CO_2Et	EtO·CO·C≡CH	Trace	—
Cl·CH_2·CH(O)CH_2	Cl·CH_2·CH(OH)·CH_2·C≡CH		
Ph·CH_2Br [i]	No low-boiling product	—	—
Ph_2C=CHBr [i]	Recovered unchanged	—	—

[a] Thompson, Burr, and Shaw, *J. Amer. Chem. Soc.*, 1941, **63**, 186. [b] Herstein, *Zhur. obshchei Khim.*, 1942, **12**, 132. [c] Oroshnik and Mebane, *J. Amer. Chem. Soc.*, 1949, **71**, 2062. [d] Bohlmann and Viehe, *Chem. Ber.*, 1954, **87**, 712. [e] Heilbron, Jones, and Weedon, *J.*, 1945, 81. [f] Jones and McCombie, *J.*, 1942, 733. [g] Cymerman and Wilks, *J.*, 1950, 1208. [h] Lespieau, *Bull. Soc. chim. France*, 1939, **6**, 947. [i] $CoCl_2$ added.

tetrahydrofuran was used resulted in the formation of a 17% yield of the acetylenic glycol, at the expense of the desired alcohol. Attempts to employ ether or benzene as solvents gave virtually no acetylenic alcohol.

The reactions of ethynylmagnesium bromide so far investigated are indicated in the

[9] Armitage, Jones, and Whiting, *J.*, 1952, 1993.
[10] Wotiz, Hollingsworth, and Dessy, *J. Amer. Chem. Soc.*, 1955, **77**, 103.

Table. For condensations with many saturated carbonyl compounds, and some αβ-ethylenic carbonyl compounds, the Grignard reagent is little if at all superior to the more easily prepared sodium or lithium acetylides. When the substance to be condensed readily polymerises (*e.g.*, cinnamaldehyde) or reacts with ammonia (chloroacetone), however, the new reagent is distinctly advantageous. The αβ-acetylenic aldehydes, in particular, could not formerly be condensed with acetylene, whereas they now give high yields of the alcohols R·C≡C·CH(OH)·C≡CH; recently a glycol, Pr·CH(OH)·C≡C·CH(OH)·C≡CH, of this type has been prepared by condensation of propiolaldehyde with (effectively) an ethynylcarbinol,[11] and these alcohols could presumably be obtained by using acetylenic hydrocarbons instead, but the present route is much more convenient. Penta-1 : 4-diyn-3-ol, an interesting and surprisingly stable compound, now becomes readily available.

Substitution of diacetylene for acetylene gave a reagent which converted acetone in 45—50% yield into the expected diacetylenic alcohol. This reaction also may have synthetical value.

Experimental

Ethynylmagnesium Bromide.—A solution of ethylmagnesium bromide was prepared under nitrogen from magnesium (4·8 g.) in dry tetrahydrofuran (140 c.c.). While still warm, this was decanted under nitrogen into a dropping funnel attached to a flask equipped with a gas inlet and a mechanical stirrer, and containing tetrahydrofuran (80 c.c.). Acetylene, freed from acetone by passage through a trap at −80°, was introduced until the liquid was saturated, and throughout the addition of the ethylmagnesium bromide solution. The latter was added in 3—5 c.c. portions, each addition being followed by a brisk frothing of the liquid which was readily distinguished from the large bubbles of acetylene, and was allowed to subside before the next addition. If the temperature of the solution fell below about 20°, crystallisation of the ethylmagnesium bromide occurred to some extent, but the resultant suspension was easily added from a dropping-funnel; at the end of the reaction the resulting solution of ethynylmagnesium bromide also was saturated at about 25°, and yielded an easily stirred suspension on cooling.

Addition of a carbonyl compound (0·14 mole) in an equal volume of tetrahydrofuran with ice-cooling, followed by stirring overnight at room temperature, decomposition of the complex with saturated ammonium chloride solution, and isolation by distillation gave the yields quoted in the cases of ethyl methyl ketone, chloroacetone, acraldehyde (experiment by Mr. Ian Bell), crotonaldehyde, and hept-2-ynal. B. p.s and refractive indices agreed with literature values, and the latter were constant to, at most, a range of 0·001. Acetophenone gave a mixture of the ethynylcarbinol and unchanged ketone, separated by chromatography on alumina, distillation of the ether–methanol eluates, and recrystallisation of the alcohol from light petroleum, giving needles, m. p. 49° (Zalkind and Ivanov [12] give m. p. 48·5—49°). Cinnamaldehyde gave a product, b. p. 90°/1 mm., which at once solidified and was crystallised from light petroleum (b. p. 40—60°), then having m. p. 67—68° (Jones and McCombie [13] give m. p. 66—67°).

1 : 1-*Diphenylbut*-3-*yn*-2-*ol.*—Diphenylacetaldehyde (8·5 g.) was treated with ethynylmagnesium bromide, as above. Isolation of the product gave a syrup which solidified and was crystallised from light petroleum (b. p. 40—60°), giving the *alcohol* as needles, m. p. 73—74° (Found: C, 86·45; H, 6·4. $C_{16}H_{14}O$ requires C, 86·45; H, 6·35%).

Penta-1 : 4-*diyn*-3-*ol.*—Ethyl formate (6 g.) in tetrahydrofuran (10 c.c.) was added at 0° to a solution of ethynylmagnesium bromide, prepared as above from magnesium (6 g.). Isolation as above and distillation gave a fraction, b. p. 80° (bath-temp.)/0·05 mm., which after crystallisation from light petroleum had m. p. 51—52° (Lespieau [14] gives m. p. 51·5—52°).

2-*Methylhexa*-3 : 5-*diyn*-2-*ol.*—A solution of ethylmagnesium bromide, prepared from magnesium (4·8 g.) in tetrahydrofuran (125 c.c.), was added during 1·5 hr. to a solution of diacetylene (12·5 g.) in tetrahydrofuran (100 c.c.) with ice-cooling under reflux (carbon dioxide–acetone). After 30 minutes' stirring acetone (8 g.) in tetrahydrofuran (10 c.c.) was added during 30 min. and the mixture was stirred overnight. Isolation of the product and distillation gave the

[11] Petrov, *Zhur. obshchei Khim.*, 1955, **25**, 1101.
[12] Zalkind and Ivanov, *Zhur. obshchei Khim.*, 1941, **11**, 803.
[13] Jones and McCombie, *J.*, 1942, 733.
[14] Lespieau, *Bull. Soc. chim. France*, 1939, **6**, 947.

diacetylenic alcohol (6·6 g., 45%), b. p. 36°/0·5 mm., n_D^{20} 1·4935 (Armitage, Jones, and Whiting [9] give b. p. 39·5°/0·5 mm., n_D^{19} 1·4938). Crystallisation of the distillation residue gave a small yield of 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol, m. p. and mixed m. p. 130—131°.

One of the authors (L. S.) thanks the Royal Norwegian Council for Scientific and Industrial Research for a Fellowship.

THE UNIVERSITY, MANCHESTER.
THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, July 5th*, 1956.]

---

931. *The Polycondensation of Benzyl Chloride catalysed by Stannic Chloride.*[1]

By L. VALENTINE and R. W. WINTER.

The kinetics of the polycondensation of benzyl chloride to form polybenzyl, catalysed by stannic chloride, have been studied. For each molecule of benzyl chloride consumed, one molecule of hydrogen chloride, the rate of evolution of which was measured, is evolved. Up to a catalyst concentration of 0·6M the rate is directly proportional to the concentration of catalyst; it then reaches a maximum at about 1·1M, and at higher concentrations becomes inversely proportional to the concentration of catalyst. Analysis of the conversion–time plots indicates that the reaction is of the first order in benzyl chloride, so that the empirical rate expression is

$$+\mathrm{d[HCl]}/\mathrm{d}t = -\mathrm{d[Ph{\cdot}CH_2Cl]}/\mathrm{d}t = k_1[\mathrm{Ph{\cdot}CH_2Cl}][\mathrm{SnCl_4}]/(1 + k_2[\mathrm{SnCl_4}]^2)$$

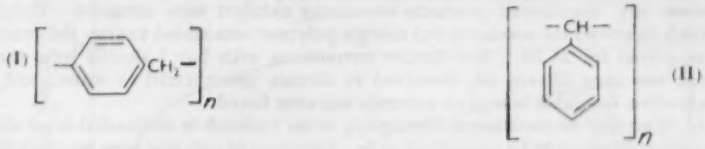
where $k_2 \sim 1{\cdot}0$. The activation energy is 7·9 kcal. per mole. The degree of polymerisation increases rapidly with extent of reaction at first, but becomes constant at extents of reaction $\geqslant 30\%$. At high conversions the degree of polymerisation is independent of temperature or concentration of catalyst. The reaction appears to be a polycondensation process proceeding by a chain reaction; probable reactive intermediates are discussed. Infrared and ultraviolet spectra of the polymers show that the structure is the same for polymers isolated at all stages of the reaction under any reaction conditions, and are consistent with the highly substituted polybenzyl structure proposed by Haas, Livingston, and Saunders.[2]

THE formation of a polymer from benzyl chloride, with the simultaneous evolution of hydrogen chloride, is an interesting example of a polycondensation process initiated by Friedel–Crafts catalysts. Such catalysts almost certainly owe their activity in vinyl polymerisations to the formation of ionic active intermediates. In view of the possibility that the polycondensation of benzyl chloride might have mechanistic affinities with ionic chain reactions, and the fact that no systematic study of the reaction had been made since modern views of polymerisation reactions were formulated, the kinetics of the reaction were investigated.

Benzyl derivatives of many different types, *e.g.*, fluoride,[3] chloride,[4] bromide,[5] and alcohol,[6] give rise to polymers that are generally called polybenzyls, although several structures have been suggested. A good summary of early work is given by Shriner and Berger [6] and also by Haas *et al.*[2] At the time this work was begun, it was thought that the polymers had a predominantly linear *para*-polybenzyl structure [6] (I), although some workers [3] preferred the pendant, or polystilbene, structure (II). Flory [7] had suggested

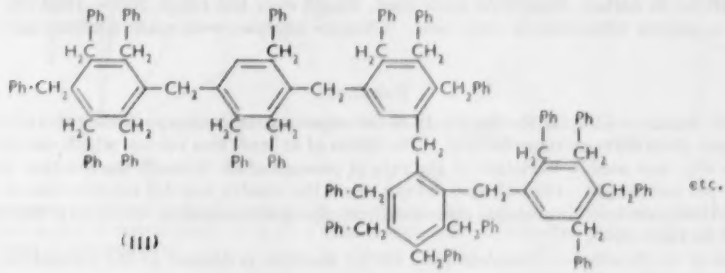
[1] A preliminary account of some of this work was presented at the International Symposium on Macromolecular Chemistry in Milan, 1954; Valentine and Winter, *Simposio Internazionale di Chimica Macromolecolare*, Supplement to *Ricerca sci.*, 1955, **25**, 95.
[2] Haas, Livingston, and Saunders, *J. Polymer Sci.*, 1955, **15**, 503.
[3] Ingold and Ingold, *J.*, 1928, 2249.
[4] Friedel and Crafts, *Bull. Soc. chim. France*, 1885, **43**, 53; Jacobson, *J. Amer. Chem. Soc.*, 1932, **54**, 1513.
[5] Boeseken, *Rec. Trav. chim.*, 1903, **22**, 312; 1904, **23**, 98.
[6] Shriner and Berger, *J. Org. Chem.*, 1941, **6**, 305.
[7] Flory, *J. Amer. Chem. Soc.*, 1952, **74**, 2718.

that the polymers might be branched polybenzyls, as reaction can occur at any of the three *ortho* and *para* positions. In the preliminary account of this work [1] it was suggested that spectroscopic data ruled out structure (I), and that accepted views of the structure might need modification. Since then, it has been suggested,[2] on the basis of spectroscopic, oxidation, and degradation data, that the polymers contain a nucleus of almost completely



substituted benzene rings and have a periphery of pendant benzyl groups (III). In view of the uncertainty as to the structure of this interesting polymer, a re-examination of the spectroscopic evidence has been made.

Although many systems of the type benzyl derivative–Friedel–Crafts catalyst give rise to identical polymers (see p. 4776), benzyl chloride–stannic chloride was preferred because the reaction mixture is homogeneous throughout the reaction, whereas some catalysts (aluminium chloride, ferric chloride) yield some polymer insoluble in any solvent.



Experimental

Stannic chloride, benzyl chloride (redistilled), *n*-butyl alcohol, and dioxan were used as supplied (B.D.H.). Redistillation immediately before use of the benzyl chloride or stannic chloride did not affect the rate of the reaction. " AnalaR " sodium hydroxide was used. The benzene used in the viscosity determinations was also " AnalaR," redistilled from a trace of alcohol.

Method of following the Evolution of Hydrogen Chloride.—The reaction was followed by measuring the amount of hydrogen chloride evolved, which is directly proportional to the amount of benzyl chloride consumed. The polycondensations were carried out in a Pyrex tube fitted with a rubber bung carrying an air bubbler; these were dried at 105° immediately before use. Benzyl chloride (10 ml.) was pipetted into the reaction tube and allowed to reach the temperature of the bath (10 min.); the catalyst was then added from a microburette and the time noted. Air, dried by bubbling through concentrated sulphuric acid, was passed through to carry off the gas evolved, which was absorbed in a vessel holding 1 l. of distilled water, fitted with a device for withdrawing 15·0 ml. samples of the solution. Complete dissolution of the hydrogen chloride was achieved by the use of a sintered-glass bubbler and rapid stirring. A constant rate of flow of air of 3 ml. per minute was used.

Samples of this solution were withdrawn and titrated with 0·01N-sodium hydroxide, bromothymol-blue being used as indicator. Readings were taken initially every two minutes at 80°, and every five minutes at 0° and 25°; occasional readings were taken up to 3—6 hr., and finally a reading was taken after 24 hr.

All reactions were carried out in a thermostat bath controlled to ±0·05°.

Isolation of Polymer.—Two methods were used, depending upon whether the reaction went to completion (Method A) or not.

Method A. Dioxan (60 ml.) was added to the reaction mixture and the resulting solution

then added drop by drop to a large excess of ice-cold water, with constant stirring, the white precipitate being filtered off and dried *in vacuo* at room temperature. The crude product contained a fraction (1—3%), insoluble in organic solvents but soluble in hydrochloric acid to give the characteristic reactions of tin, which was filtered off before the polymer was reprecipitated from a solution in dioxan and dried as above.

Method B. Method A proved unsatisfactory if the polymer was isolated at low extents of reaction, when oily, discoloured products containing catalyst were obtained. Butyl alcohol (25 ml.), which dissolved the reactants but not the polymer, was added to stop the reaction, and the mixture stirred for 24 hr.; two further extractions with butyl alcohol were then made. The polymer was then filtered off, dissolved in dioxan, precipitated in water, and dried as above; no fraction insoluble in organic solvents was ever found.

General.—Viscosity measurements were made in an Ubbelohde suspended-level viscometer, modified to allow dilutions to be carried out in it. Solutions of polymer were made up in benzene and filtered through a No. 3 or 4 sintered-glass crucible; reproducibility was better if a No. 4 filter was used. The concentration of the final stock solution was determined by evaporation of the solvent.

Ultraviolet absorption spectra were determined on a Unicam spectrophotometer, chloroform as solvent and 1 cm. cells being used. Infrared absorption spectra were determined by Dr. J. H. Towler and Mr. B. H. Holland, of the University of Leeds, using a Grubb-Parsons single-beam instrument, or by Dr. E. Rothstein, also of the University of Leeds, using a Grubb-Parsons double-beam instrument, both with sodium chloride prisms. Over the range 1650—650 cm.$^{-1}$, 10% solutions in carbon disulphide were used, whilst over the range 2000—1650 cm.$^{-1}$, 50% solutions in carbon tetrachloride were used. Chlorine analyses were made commercially.

Results

Kinetic Studies.—Despite the simplicity of the experimental techniques, the rates of evolution of hydrogen chloride were reproducible. The mean of at least two values, which usually agreed to within 5%, was used. Variation of the rate of passage of air through the reaction tube from 1 to 5 ml. per minute (30—160 bubbles) did not affect the results, nor did substitution of nitrogen for air. Under certain conditions, glass catalyses the polymerisation of aralkyl halides,[8] but we found no such effect.

Course of the Reaction.—Complete (*i.e.*, 100%) reaction is defined as the theoretical yield of hydrogen chloride in the reaction

$$n\mathrm{C_7H_7Cl} \longrightarrow (\mathrm{C_7H_6})_{n-1}{\cdot}\mathrm{C_7H_7Cl} + (n-1)\mathrm{HCl}, \text{ where } n = 1000$$

From this equation, 10 ml. of monomer (*d* 1·105), the amount always taken in this work, would give the yields of polymer and hydrogen chloride in Table 1 for various degrees of polymerisation.

Table 1

Degree of polymerisation	2	4	6	10	17	52	1000
Amount of HCl (g.)	1·59	2·58	2·66	2·87	3·00	3·13	3·19
Amount of polymer (g.)	9·45	8·65	8·36	8·17	8·06	7·93	7·86

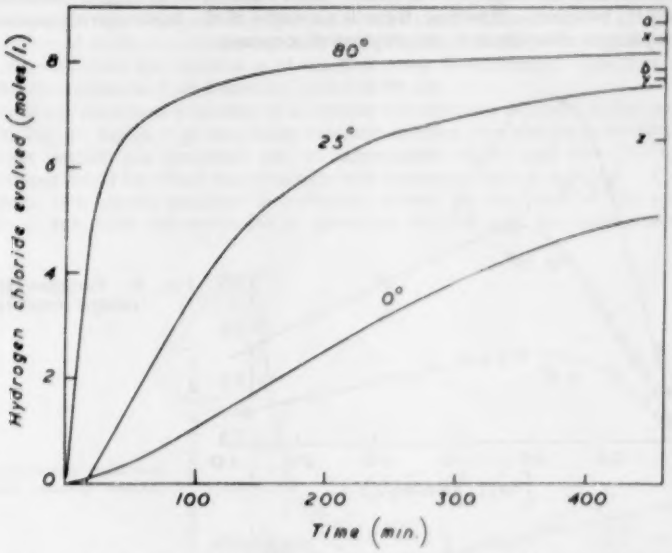
At 0°, a faint straw colour appears within 30 sec.; at higher temperatures the interval is shorter. No gas is evolved until the solution is orange. The colour intensifies throughout the reaction, and is deep red after about 12% reaction. The viscosity also increases and by 60—70% reaction the reaction mixture is a dark reddish-brown semi-solid mass expanded by bubbles of hydrogen chloride. Despite the great alterations in the nature of the reaction medium, the evolution of hydrogen chloride was smooth and continuous until reaction was complete.

Typical reaction curves at 0°, 25°, and 80°, for use of 0·165M-stannic chloride, are shown in Fig. 1. At all temperatures there is a short induction period (0—4% reaction) followed by an extensive period (4—40% reaction) over which the rate is practically constant, and finally by a continuous decrease in rate until the end. If a further 10 ml. of benzyl chloride were added to a reaction that had reached 56% conversion and was showing the normal rapid decrease in rate, another long period of constant rate (80% of the initial constant rate) was found. This shows that consumption of catalyst must be very small.

[8] Olivier and Wit, *Rec. Trav. chim.*, 1938, **57**, 1117.

A satisfactory mass balance between monomer and yield at 24 hours' reaction of polymer and hydrogen chloride was achieved (see Table 2). The sum of the weights of polymer plus hydrogen chloride is always 3—7% less than the weight of monomer introduced, probably

FIG. 1. *Course of reaction at various temperatures for* $[SnCl_4]$ = 0·165M.



a, *b*; Theoretical yields of hydrogen chloride for 100% reaction to form polymers of degree of polymerisation ∞ and 10 respectively. *x*, *y*, *z*; Yields of hydrogen chloride after reaction for 24 hr. at 80°, 25°, and 0° respectively.

FIG. 2. *Residual monomer as a function of extent of reaction at 25° and* $[SnCl_4]$ = 0·165M.

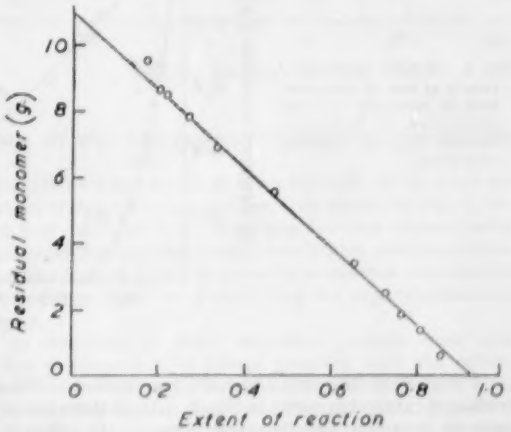


TABLE 2.

Temp.	$[SnCl_4]$	Yield (g.) Polymer	HCl	Total	Temp.	$[SnCl_4]$	Yield (g.) Polymer	HCl	Total
0°	0·165	7·80	2·70	10·50	70°	0·165	7·60	3·05	10·65
0	0·325	7·31	2·90	10·21	80	0·165	7·47	3·05	10·52
25	0·165	7·75	2·73	10·48	Theoretical for 100% reaction		7·86	3·19	11·05

owing to hydrogen chloride remaining in the reaction mixture, a loss of low molecular-weight polymers in the precipitations, and, at high temperatures, volatilisation of benzyl chloride.

The residual monomer at various extents of reaction was estimated by subtracting the sum of the weights of polymer and hydrogen chloride from the weight of monomer originally present. As shown in Fig. 2, the amount of monomer decreases linearly with extent of reaction; under these conditions ($[SnCl_4]$ = 0·165M, 25°) the evolution of hydrogen chloride does not exceed about 91% reaction. However, there is no doubt of the linear correspondence between evolution of hydrogen chloride and consumption of monomer.

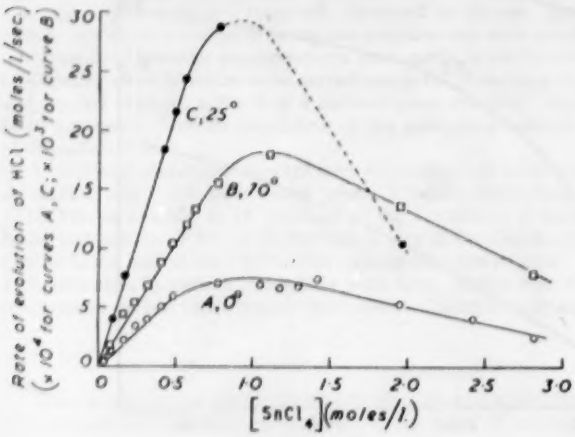


FIG. 3. *Variation of rate with catalyst concentration.*

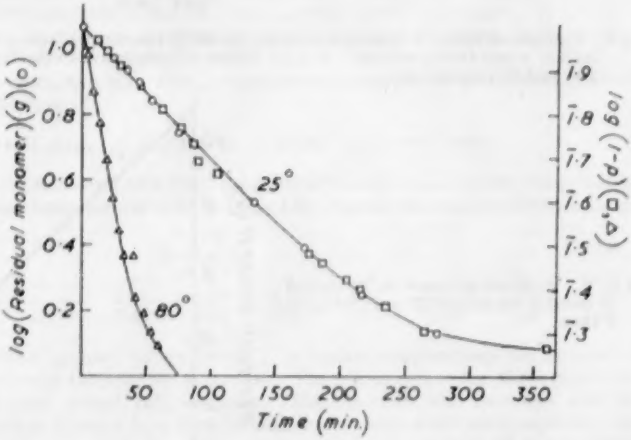


FIG. 4. *Kinetic analysis of results of rate of consumption of monomer* (○) *and evolution of hydrogen chloride* (□, △). $[SnCl_4]$ = 0·165M.

Variation of Rate with Catalyst Concentration.—The effect on the rate of varying the concentration of catalyst is shown in Fig. 3. At all three temperatures the rate of evolution of hydrogen chloride is at first directly proportional to the catalyst concentration (0 to 0·6M), then reaches a maximum when the concentration of stannic chloride is about 1·0M, and thereafter declines. The rate at high concentrations of catalyst at 0° is inversely proportional to the catalyst concentration, and although there are fewer data at the higher temperatures, the general similarity of the curves makes it probable that a similar inverse relationship exists.

No account has been taken in Fig. 3 of the dilution of monomer by catalyst; for example, at the very highest concentration of catalyst used, the monomer concentration is only 5·82M, compared with 8·74M for pure benzyl chloride. Even if this decrease is allowed for (on the

assumption that the rate is of either first or second order in monomer concentration), the maximum is still found, although at a greater concentration of catalyst.

Order of Reaction with Respect to Monomer.—No experiments at varying concentration of monomer were made, but the kinetic order can be deduced from data on the extent of reaction as a function of time. The rate equation for a first-order reaction is $-kt = \ln M/M_0 = \ln (1 - p)$, where k is the rate constant, t the time, M_0, M the concentrations of reactant initially and at the time t, respectively, and p the fractional extent of formation of products. A plot of the logarithm of residual monomer against time (Fig. 4) is linear over a wide range (0—75% reaction), showing that the reaction is of the first order in monomer. The results have been corrected for the existence of an induction period of 26 min.

Analysis of the results of evolution of hydrogen chloride also indicates a first-order reaction, as shown in Fig. 4; $\log (1 - p)$ is a linear function of time over the range 0—60% reaction, if the induction periods are corrected for, in experiments at 25° and 80° ($[SnCl_4] = 0{\cdot}165$M). Similar analyses result for other temperatures and concentrations of catalyst. The agreement between these two kinetic analyses is strikingly shown by the plots of the results for the experiment at 25°, both the evolution of hydrogen chloride and the consumption of benzyl

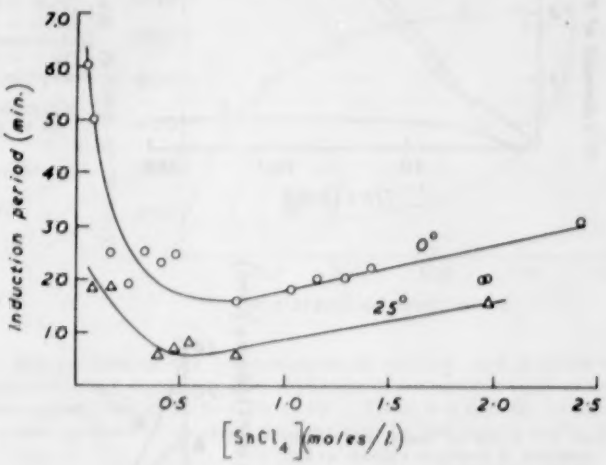


FIG. 5. *Variation of induction period with catalyst concentration.*

chloride fitting the same first-order plot. At very high degrees of conversion, a second-order plot fitted the results better.

The Induction Period.—Induction periods were estimated as the intercepts on the time axis of the linear portions of the plots of extent of reaction against time. As shown in Fig. 5, at a given temperature the induction period first decreases with increasing catalyst concentration, is afterwards virtually independent of the concentration, and finally at very high catalyst concentrations increases again. This is almost the inverse of the relation between rate and catalyst concentration. At 70° the induction period is so short (1—3 min.) that the experimental error is too large for any conclusions to be drawn.

Various experiments were made to ascertain if these induction periods were real. Spectrophotometric investigations of the development of colour revealed that the optical density initially increased almost linearly with time and then at an accelerating rate, until evolution of hydrogen chloride made further readings impossible. The induction periods in these experiments (in loosely stoppered test-tubes) were almost exactly the same as those found in the standard apparatus, suggesting that the induction periods are real. Benzyl chloride presaturated with dry hydrogen chloride gave no induction period, as shown in Fig. 6, but the desorption of monomer saturated with hydrogen chloride, but free from catalyst, had an induction period of about 10 min. It is difficult to reconcile these results. Most of the evidence, including that on the reaction between stannic chloride and polymer (p. 4776), supports the view that the induction periods are real, although the true kinetic induction periods may be shorter than the measured values.

Activation Energy.—Activation energies were calculated from the results represented in Fig. 3. As long as the rate is first-order in catalyst concentration, the activation energy (E) is 8·1 kcal. per mole, but there is a slight tendency for it to increase at high catalyst concentrations, as shown by the following figures (E in parentheses following stannic chloride molarity) 0—0·60 (8·1), 0·77 (8·2), 1·00 (8·2), 1·95 (8·6), 2·81 (9·0).

Effect of Water.—Water is often an essential cocatalyst in Friedel–Crafts polymerisations,[9] but

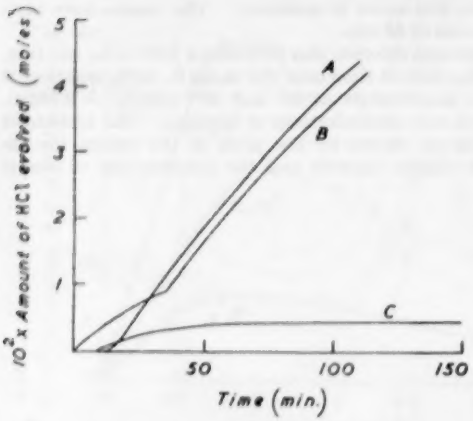


FIG. 6. *Effect of presaturation of benzyl chloride with hydrogen chloride on induction period at 25°.*

A; [HCl] = 0, [$SnCl_4$] = 0·165M (control).
B; [HCl] = saturated, [$SnCl_4$] = 0·165M (polymerisation).
C; [HCl] = saturated, [$SnCl_4$] = 0 (loss or desorption).

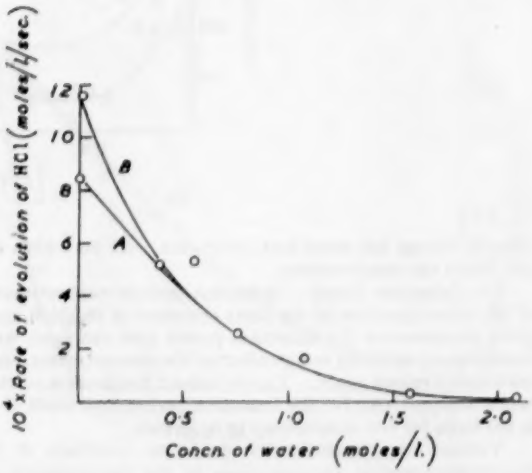


FIG. 7. *Effect of water on rate of evolution of hydrogen chloride at 25°.* [$SnCl_4$] = 0·165M.

A, Ordinary benzyl chloride.
B, Benzyl chloride dried over anhydrous calcium sulphate.

in the present reaction it appears to have merely a retarding effect, as shown in Fig. 7. Redistillation of the monomer immediately before use did not affect the rate, but redistillation followed by drying with anhydrous calcium sulphate for 16 hr. caused a 35% increase in rate. The general course of the reaction was exactly the same at all concentrations of water, even the slowest rates suffering a further decrease at long times of reaction, although the extent of reaction was less than 5%. Even when sufficient water had been added to form stannic chloride pentahydrate, the rate was still 27% of the value in the absence of water, although the solid

[9] Evans and Polanyi, *J.*, 1947, 252; Pepper, *Quart. Rev.*, 1954, **8**, 100.

pentahydrate had no catalytic effect whatever. The induction periods were unaffected by the presence of water.

Molecular-weight Measurements.—The limiting viscosity number was taken as a measure of the molecular weight, Bezzi's relation [10] between the cryoscopic molecular weight (M) and the viscosity of benzene solutions of polymer, prepared with aluminium chloride as catalyst, being used, *viz.*, $(\eta_i - \eta_0)/\eta_0 c = 4{\cdot}01 \times 10^{-4}M$, where η_i, η_0 are the viscosities of solution and solvent, respectively, and c is the concentration in base moles per litre. In the units now approved,[11] $(\eta_i - \eta_0)/\eta_0 c = 4{\cdot}46 \times 10^{-2}M$, where c is now in g. per ml. Bezzi apparently measured the viscosity number $[(\eta_i - \eta_0)/\eta_0 c]$ in the range $c = 0{\cdot}01$—$0{\cdot}03$ g. per ml.; in this work, the data were extrapolated to zero concentration, but the limiting viscosity numbers ($[\eta]$) so obtained do not differ from the viscosity numbers at $c = 0{\cdot}01$—$0{\cdot}03$ g. per ml. by more than 8%. As the viscosity ratio (η_i/η_0) was never greater than 1·8, even for 10% solutions, the experimental error in measuring the viscosity number is rather high.

In Table 3 the results of the viscosity measurements are summarised; all the polymers were obtained after 24 hours' reaction.

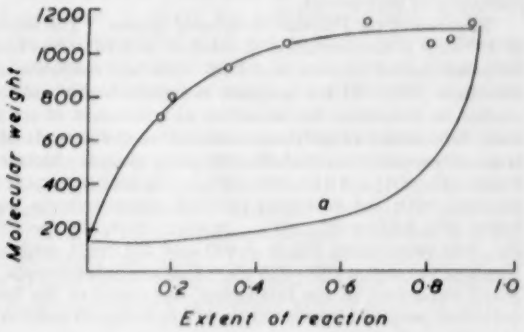


FIG. 8. *Variation of molecular weight with extent of polymerisation at 25°.* $[SnCl_4] = 0{\cdot}165M$.

a, Theoretical curve for a polycondensation mechanism.

The molecular weight is independent of the concentration of catalyst, and practically independent of the temperature, although there may be a slight rise in molecular weight as the temperature is increased, from about 1000 at 0° to 1150 at 70°. There is a definite increase in molecular weight with increasing extent of reaction, as illustrated by the results in Fig. 8.

TABLE 3. *Viscosity and molecular-weight determinations.*

$[SnCl_4]$	0°			25°			70°		
(moles/l.)	$[\eta]$	M	k'	$[\eta]$	M	k'	$[\eta]$	M	k'
0·084	4·0	900	1·55	—	—	—	5·2	1190	0·86
0·165	—	—	—	4·6	1030	1·33	5·07	1140	0·95
0·246	—	—	—	5·34	1200	0·66	—	—	—
0·325	—	—	—	—	—	—	5·45	1220	0·84
0·478	4·2	940	1·65	4·88	1100	1·15	—	—	—
0·769	4·2	940	1·70	—	—	—	5·1	1140	0·95
1·10	—	—	—	4·94	1110	1·18	—	—	—
1·41	5·04	1130	1·08	—	—	—	5·25	1180	0·87
1·95	—	—	—	5·10	1150	1·10	—	—	—
2·42	4·6	1030	1·35	—	—	—	4·68	1050	1·08
Mean	4·4	990	1·47	5·0	1120	1·08	5·1	1160	0·92

At an extent of reaction of about 30—40%, however, the molecular weight becomes independent of the conversion.

As all the plots of viscosity number against concentration were linear, up to concentrations of 0·1 g. per ml., they were interpreted in terms of Huggins's equation $(\eta_i - \eta_0)/\eta_0 c = [\eta] + k'[\eta]^2 c$

[10] Bezzi, *Gazzetta*, 1936, **66**, 491.
[11] Report of Commission on Macromolecules of I.U.P.A.C., *J. Polymer Sci.*, 1952, **8**, 257.

From the values of k' listed in Table 3, there appears to be a fall in the value of k' as the temperature of the polycondensation is raised. There is a wide scatter in the values of k', however, because of its extreme sensitivity to changes in the value of $[\eta]$ for small values of $[\eta]$.

Reaction between Stannic Chloride and Polymer.—As mentioned above, an intense red colour develops during the reaction. Similar colours are often found in Friedel–Crafts reactions, *e.g.*, the aralkylation of benzene with benzyl chloride,[12] but in the present reaction the colour may be partly due to reaction between polymer and catalyst. Solutions of the pure polymer in benzene, chloroform, ethylene chlorohydrin, or mesityl oxide give intense red colours as soon as stannic chloride is added, which fade slowly. Aluminium chloride and sulphuric acid give similar effects, and both stannic chloride and aluminium chloride cause a similar colour reaction with solid polybenzyl. No simple benzene derivatives gives a red colour with stannic chloride, although several give a pale yellow colour. (Benzene, toluene, chlorobenzene, and polystyrene give no colour at all.) If stannic chloride is added to a solution of purified polybenzyl in benzyl chloride, an intense red colour develops instantaneously. The red colour persisting throughout the reaction may then be due to interaction between polymer and catalyst, and the slow development of colour in the induction periods is probably associated with the slow initial formation of polybenzyl.

Structure of the Polymer.—Infrared spectra. The infrared spectrum of a polybenzyl prepared at 25° with a concentration of catalyst of 0·165M has been reproduced.[1] Other workers [2] have obtained similar spectra, and from these and oxidative studies proposed the highly substituted structure (III). If the polymer is indeed highly substituted, it is important for the kinetic studies to determine the structure as a function of conversion. Accordingly, infrared spectra were determined of polymers isolated at the extents of reaction at 25° shown in parentheses from polymerisations with the following stannic chloride molarities: 0·165M (10, 25, 65, 75%), 0·40M (25, 40%), 1·41M (30, 75%). In addition, polymers isolated after virtually complete reaction with the following catalyst concentrations and temperatures were also examined: 0·33M (0°), 0·165M (25°, 80°). In every case, the spectra showed essentially the same features, *viz.*, two very strong bands at 697 and 727 cm.$^{-1}$, with an inflection at 743 cm.$^{-1}$, and no other bands in the region 700—820 cm.$^{-1}$ that are characteristic of other types of aromatic substitution. Small variations in the intensities, but never in the frequencies, of the bands occurred. The polymers prepared by the action of concentrated sulphuric acid on benzyl alcohol, or aluminium chloride on benzyl bromide, also have the same infrared spectrum and presumably the same structure.

The spectra were also determined in the region 1650—2000 cm.$^{-1}$, which usually affords one of the best methods for the identification of benzene-ring substitution. However, the results were inconclusive. All polymers showed three bands at 1970, 1930, and 1885 cm.$^{-1}$, of gradually diminishing intensity as the frequency is reduced, followed by a strong band at 1810 cm.$^{-1}$. This pattern differs from all the standard types listed by Young *et al.*,[13] but is not inconsistent with a structure composed of both highly substituted and monosubstituted rings.

Ultraviolet spectra. The ultraviolet spectra of two polymers prepared by using stannic chloride as catalyst have already been reproduced.[1] The main feature is a broad absorption band over the region 250—290 mμ, with three small peaks at 264, 266, and 270 mμ, the last being the main peak. Polymers prepared at 0°, 25°, and 80°, at various catalyst concentrations, all have the same spectrum, and the specific extinction coefficient, E [(optical density)/(path length in cm.)(concn. in g. per l.)], is 5·1—5·7. Polybenzyls prepared from benzyl alcohol or benzyl bromide have very similar spectra, although the extinction coefficients are somewhat higher.

Discussion

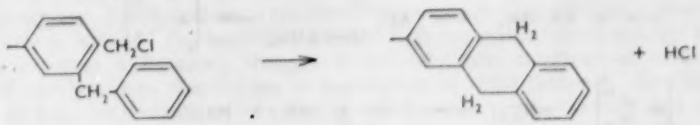
Structure of the Polymer.—Our infrared results almost completely agree with those of Haas and his co-workers, in that there is no evidence of any type of benzene substitution other than monosubstitution in the characteristic region 700—850 cm.$^{-1}$. As polymers of virtually identical infrared spectra were obtained with a wide variety of initiators and benzyl monomers (in addition to those studied by us, the systems benzyl chloride–ferric oxide and benzyl fluoride–sulphuric acid also give polymers of identical spectra [2]), it seems

[12] Steele, *J.*, 1903, **83**, 1470.
[13] Young, duVall, and Wright, *Analyt. Chem.*, 1951, **23**, 709.

that all benzyl derivatives give polymers of essentially the same structure, no matter what catalyst is used. (This applies only to soluble polymers; some systems give insoluble polymers whose structures have not been determined.) The main difference between the present work and the previous infrared studies is that we find only two bands (at 697 and 727 cm.$^{-1}$, infl. at 743 cm.$^{-1}$), whereas Haas *et al.* report three bands, at 675, 695, and 725 cm.$^{-1}$. (The actual wave numbers were not quoted in the paper, but have been read from a spectrum kindly provided by Dr. H. C. Haas, whom we thank.) It is not clear why the band at 675 cm.$^{-1}$, which is attributed to a rocking vibration of the methylene group, should be absent in our polymers, but neither analyst found any trace of it. It is significant that the polymer has the same structure at all stages of the reaction, at least from 10% reaction onwards, as shown by the identity of the spectra in the regions 700—850 cm.$^{-1}$ and 1650—2000 cm.$^{-1}$.

The ultraviolet absorption spectra of all the polymers were also virtually indistinguishable. Although the general shape of the spectra is in accord with that expected for structure (III), the magnitude of the extinction coefficient is not. Monosubstituted benzenes generally have values of E of about 2, whilst the polybenzyls have values of 5 to 6. *para*-Substitution is usually the only type that gives rise to extinction coefficients of this magnitude for unconjugated hydrocarbon substituents, but in view of the strong evidence against *para*-substitution, the high absorption must be attributed to other, unknown, causes.

Unequivocal proof of the structure has not yet been attained, but as structure (III) provides the best explanation of the widest range of data, the discussion of the mechanism will be made on the assumption that the polymer has this structure, although the presence of small amounts of other structures cannot be ruled out. Chlorine contents of polymers prepared at various temperatures and catalyst concentrations ranged from 0·5 to 3·0% and showed no obvious dependence on either variable. The average value was about 1%, corresponding to the termination of only one polymer molecule in three by a chloride atom. The terminal chlorine atom may react with a side-chain benzyl group to form a dihydroanthracene derivative, *e.g.*,



Such terminal groups would probably not be detected in either the infrared or the ultraviolet spectra. Cyclisation reactions of this type may also explain why in some reactions (see, *e.g.*, experiments at 70° and 80° in Table 2 and Fig. 1) the yield of hydrogen chloride is greater than that expected for polymers of a degree of polymerisation of about 12.

Mechanism of the Reaction.—The results given above show unequivocally that the mechanism is not of the normal polycondensation type, in which the degree of polymerisation increases as the reaction proceeds in accordance with the equation: Degree of polymerisation $= 1/(1 - p)$. As shown in Fig. 8, the molecular weight of the polymer becomes constant after 30% reaction. The behaviour expected in a stepwise polycondensation, shown in the same diagram, bears no resemblance to the experimental results. Attainment of a constant molecular weight early in the reaction is typical of chain polymerisations.

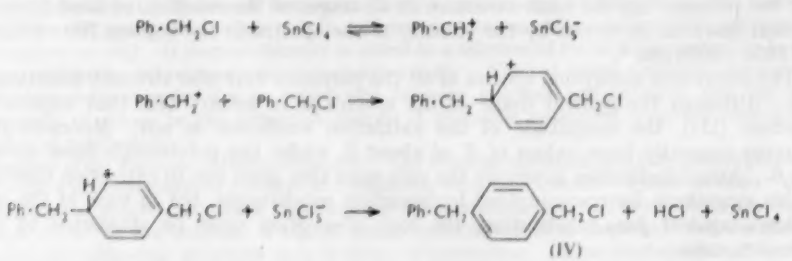
It has been suggested [14] that the molecular weights may be invalid because the degree of branching of the polymer may increase with extent of reaction. However, as the polymers have the same structure at all stages of the reaction and irrespective of the catalyst used, they would all be expected to satisfy the same relation between limiting viscosity number and molecular weight. The molecular weights are very low—too low, in fact, to permit the high degree of substitution and branching demanded by structure (III)—and Bezzi's

[14] Frank, *Simposio Internazionale di Chimica Macromoleculare*, supplement to *Ricerca sci.*, 1955, **25**, 109.

calibration may be in error. This would not affect our conclusions, but merely the absolute values of the molecular weights.

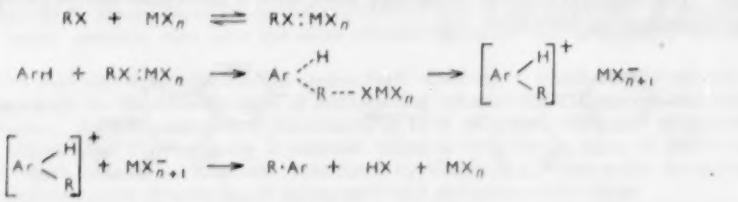
Another criterion of a normal polycondensation is that the weight-fraction of monomer at any stage is given by $(1 - p)^2$, whereas for addition polymerisations the weight fraction is simply $(1 - p)$. It is obvious from Fig. 2 that a stepwise polycondensation is ruled out.

The reaction is undoubtedly in many ways a typical Friedel–Crafts one, the main complications arising from the polymeric nature of the product. When this work was begun, we thought the reaction probably involved benzyl cations, *e.g.*,



(IV)

Polymers may readily be formed by reactions such as these on the dimer, trimer, etc. This view of the reaction was in harmony with the then accepted picture of Friedel–Crafts reactions. Since then, however, H. C. Brown has suggested (see, *e.g.*, reference 15) that in the alkylation of aromatic compounds by primary halides, an un-ionised complex between the catalyst and the alkyl halide is involved, *e.g.*,

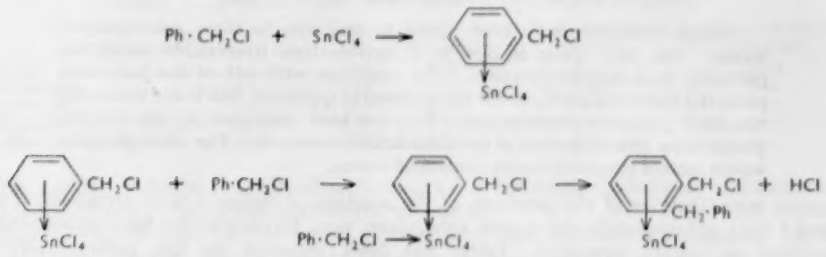


Brown and Wallace [16] have shown that the kinetics of the reaction of 3 : 4-dichlorobenzyl chloride with benzene are incompatible with the ionisation mechanism, but are in agreement with those expected from the displacement mechanism. A similar reaction scheme can be applied to the autocondensation of benzyl chloride, if further benzylation of the primary product (IV) is allowed for. [If structure (III) is accepted as correct, reactions involving the attack of the chloromethyl group of the polymer on monomer can be largely eliminated, as these could not lead to a highly substituted structure.]

However, it is difficult on either of these reaction schemes to explain the chain character of the mechanism. Haas *et al.* have suggested that after the formation of the dimer, subsequent benzylation is much more rapid. In terms of a chain reaction, the formation of the dimer may be regarded as the initiation step (slow), which is followed by the propagation steps of benzylation of the nuclear positions of the dimer (rapid). The termination step may be non-existent in that the reaction may simply stop when all the nuclei of the dimer are substituted. It may be significant that all the molecular weights correspond to that of the completely substituted dimer (1025). The amorphous nature of the product, however, and its mechanical behaviour suggest that it is a mixture of polymers.

[15] Brown, Pearsall, Eddy, Wallace, Grayson, and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 1462.
[16] Brown and Wallace, *ibid.*, p. 6285.

Such a reaction might take place by way of either benzyl cations or complexes of monomer with stannic chloride, the latter possibly being π-complexes, *e.g.*,



The complex between dimer and catalyst could then be further substituted, and so on. The chain would be terminated by elimination of the catalyst. Any mechanism must allow for regeneration of catalyst, which was demonstrated by the effect of adding fresh monomer to a partially reacted mixture (p. 4770). Each molecule of catalyst must be capable of converting about 100 monomer molecules into ten polymer molecules, since a catalyst concentration of 0·08M is sufficient to convert completely 8·74M-benzyl chloride into decamer.

However, the exact nature of the reaction will probably be elucidated only when ordinary Friedel–Crafts reactions are better understood.

At high concentrations of catalyst, additional complications arise. The empirical rate expression that fits the data at all temperatures and concentrations of catalyst is :

$$+\mathrm{d[HCl]}/\mathrm{d}t = k_1[\mathrm{SnCl_4}][\mathrm{M}]/(1 + k_2[\mathrm{SnCl_4}]^3)$$

Since the maximum of the rate–catalyst concentration curve occurs at $[\mathrm{SnCl_4}] \sim 1{\cdot}0$M at all temperatures, differentiation of the above expression and substitution of $[\mathrm{SnCl_4}] = 1{\cdot}0$ yields a value of k_2 of 1. The inhibiting effect of high concentrations of catalyst is perhaps analogous to other well-kmown changes in Friedel–Crafts reactions at molar concentrations of catalyst, *e.g.*, the change in orientation of substitution.[17] As the polymer prepared at high concentrations of catalyst still has the same structure and molecular weight, the mechanism is probably essentially the same. Stannic chloride may form two complexes, only one of which is active, the inactive form being favoured at high concentrations of catalyst.

The authors thank Dr. E. Rothstein, Dr. J. H. Towler, and Mr. B. H. Holland for infrared spectra. One of them (R. W. W.) is indebted to the British Rayon Research Association for a Technological Scholarship.

Department of Textile Industries,
The University, Leeds 2.

[*Received, June 25th,* 1956.]

[17] Norris and Rubinstein, *ibid.*, 1939, **61**, 1163.

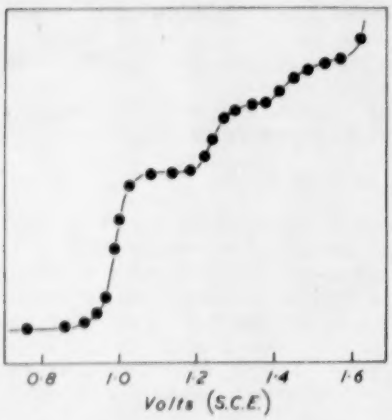
932. *The Polarography of Some Simple Pyrazine Derivatives.*

By L. F. Wiggins and W. S. Wise.

Simple pyrazines have been found to give rise to three polarographic waves. The first wave is due to a two-electron irreversible reduction, probably to a dihydropyrazine. The variation with pH of the half-wave potential indicates a pK_a of 3·6 for tetramethylpyrazine, but lower values for the other pyrazines investigated. This has been confirmed by the spectrophotometric determination of the dissociation constants. The other pyrazine waves are not simple diffusion-controlled waves.

During investigations of the products of the reaction of molasses with ammonia, it was found [1] that polarographically active substances were formed which were subsequently identified as simple pyrazines. Little has been reported on the polarography of pyrazines,[2,3] and the polarographic behaviour of some simple derivatives has therefore been examined.

The pyrazines investigated gave polarographic reduction waves over a wide range of pH. In pure solutions there were very pronounced maxima but these were easily eliminated by the addition of gelatin. A typical polarogram is shown in the Figure for tetramethylpyrazine



Polarogram of tetramethylpyrazine in M*-phosphate buffer of* pH 6·9 *containing* 0·004% *of gelatin.*

in a phosphate buffer of pH 6·9. Three waves can be distinguished. The first wave, *i.e.* that at the most positive potential, remained unchanged in height over a wide range of pH for a given pyrazine concentration. The heights of the second and the third wave were dependent on the pH of the solution. At pH about 1, the two waves became merged and the total wave height was roughly equal to that of the first pyrazine wave. As the pH was increased, the heights of the second and the third wave decreased until by pH 9 they had disappeared. The other pyrazines investigated behaved similarly.

The First Pyrazine Wave.—The height of the first pyrazine wave was proportional to the pyrazine concentration (0·1—10 mM) for all the pyrazines investigated, and the limiting currents were not affected by the gelatin concentration, below 0·05%, when the pH of the solutions was below 7. In more alkaline solutions the wave became badly shaped and the limiting current decreased slightly with increasing gelatin concentration. The wave height was approximately proportional to the square root of the height of the mercury reservoir so that it is a normal diffusion-controlled wave.

[1] Wiggins and Wise, *Chem. and Ind.*, 1955, 656.
[2] Bonito, *Pontif. Acad. Sci. Acta*, 1945, **9**, 65.
[3] Mader and Frediani, *Analyt. Chem.*, 1948, **20**, 1199; Rickes, Trenner, Conn, and Keresztesy, *J. Amer. Chem. Soc.*, 1947, **69**, 2751; Allen, Pasternak, and Seaman, *ibid.*, 1952, **74**, 3264.

Values for the diffusion-current constant, I_d, as defined by Lingane,[4] are given in Table 1.

TABLE 1. *Diffusion-current constants of pyrazine derivatives.*

Pyrazine	*M*	0·5N-HCl	M-Phosphate buffer, pH 3·06	M-Acetate buffer, pH 4·39
2-Methyl-	94	3·83	3·73	3·59
2 : 5-Dimethyl-	108	3·70	3·46	3·42
Tetramethyl-	136	3·45	3·26	3·16
5-(D-*arabo*Tetrahydroxybutyl)-2-methyl-	213	2·98	2·89	2·83
2 : 5-Bis-(D-*arabo*tetrahydroxybutyl)- ...	320	3·19	2·80	2·71

The number of electrons involved in the reaction at the dropping-mercury electrode was established as two by using the coulometric technique.[5]

Logarithmic analyses of the waves did not give the slopes (0·030) expected for an ordinary two-electron reduction, and the slope was dependent on pH, as shown for example by the results for tetramethylpyrazine in Table 2. It is therefore evident that the first

TABLE 2. *Variation of slope of log plot with* pH *for tetramethylpyrazine.*

pH	1·3	2·7	3·3	4·7	6·2	7·3
Slope of log plot	0·049	0·049	0·046	0·042	0·033	0·031

pyrazine wave represents an irreversible two-electron reduction. The most likely reaction product is a dihydropyrazine.

Dissociation Constants of the Pyrazines.—Four of the pyrazine derivatives investigated gave a linear relation between half-wave potential and pH of the form $-E_{\frac{1}{2}} = E_0 + 0{\cdot}085$pH. Values of E_0 for the different pyrazines were: 2-methyl, 0·32; 2 : 5-dimethyl, 0·35; 5-(D-*arabo*tetrahydroxybutyl)-2-methyl, 0·34; 2 : 5-bis-(D-*arabo*tetrahydroxybutyl), 0·34. The half-wave potentials of these pyrazines were therefore almost identical at all pH values. Tetramethylpyrazine behaved differently, and its half-wave potential can be expresssed as $-E_{\frac{1}{2}} = 0{\cdot}48 + 0{\cdot}059$pH below and as $-E_{\frac{1}{2}} = 0{\cdot}38 + 0{\cdot}087$pH above pH 3·6.

The variation of the half-wave potential of pyrazines with pH indicates that hydrogen ions are involved in the electrode reduction, as would be expected if the reduction product is a dihydropyrazine, although the theoretical slope of 0·059 is only found for tetramethylpyrazine below pH 3·6. The results for this pyrazine suggest that it has a pK_a of 3·6; below pH 3·6 the salt is reduced and above pH 3·6 the free base. The other pyrazines did not appear to form salts at a pH within the range of the polarographic investigation.

The dissociation constants of the pyrazines investigated have not been recorded, although that of pyrazine itself is known.[6] The ultraviolet absorption spectra of pyrazine in sulphuric acid solutions [7] suggested that the dissociation constants could be measured spectrophotometrically,[8] and it was in fact found that the spectra of the salt form and of the free base were sufficiently different. As expected,[7] the absorption peak of the former was always at a higher wavelength than that of the latter. The wavelengths of the peaks and pK_a values are given in Table 3, which shows that the pyrazines are very weak bases. The pK_a is increased by the successive introduction of methyl groups, but the tetrahydroxybutyl side-chain has no influence. Tetramethylpyrazine is the only one investigated having a pK_a within the region where an inflexion is evident in the curve connecting half-wave potential with pH. The value of the dissociation constant of tetramethylpyrazine obtained spectrophotometrically agrees well with the value suggested by the polarographic measurements.

The spectrum of 3 : 6-di*iso*butyl-2-hydroxypyrazine was also determined. As will be seen from the absorption peaks, this compound differs markedly from the other pyrazines. Moreover, there was a further variation in the spectra for alkaline solutions; this difference was not large but corresponded to an ionisation at pH 10, probably due to the ionisation of

[4] Lingane, *Ind. Eng. Chem. Anal.*, 1954, **15**, 588.
[5] Wise, unpublished results.
[6] Albert, Goldacre, and Phillips, *J.*, 1948, 2240.
[7] Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711.
[8] Beale, *J.*, 1954, 4494.

the hydroxy-group. There is, however, the possibility of tautomerism in 2-hydroxypyrazines, as has been found for the analogous pyrimidine and pyridazine derivatives.[9,10]

The Other Pyrazine Waves.—These were not investigated in great detail as they were found not to be simple diffusion-controlled waves. Their heights were not accurately proportional to pyrazine concentration and were affected by the concentration of gelatin. In solutions of higher pH, where the wave heights were comparatively small, they became

TABLE 3. *Absorption peaks and* pK_a *values of pyrazines.*

Pyrazine	Salt, mμ	Free base, mμ	pK_a
Unsubstituted	—	—	0·6
2-Methyl-	280	270	1·4
2 : 5-Dimethyl-	290	275	1·9
Tetramethyl-	300	double peak	3·7
5-(D-*arabo*Tetrahydroxybutyl)-2-methyl-	285	275	1·4
2 : 5-bis-(D-*arabo*Tetrahydroxybutyl)-	290	275	0·7
3 : 6-Di*iso*butyl-2-hydroxy-	350	330	1·7

TABLE 4. *Dependence of wave heights on mercury pressure.*

Pressure, cm.	66	47	36	31
First wave, μA	4·7	3·8	3·4	3·0
Second wave, μA	1·9	1·8	1·8	1·7
Third wave, μA	1·0	1·0	0·9	0·9

independent of the height of the mercury reservoir. This is illustrated (Table 4) for a solution which contains $5{\cdot}3 \times 10^{-4}$M-tetramethylpyrazine and 0·004% of gelatin in M-phosphate buffer of pH 6·9. This behaviour is typical of waves controlled kinetically;[11] such waves are often found for heterocyclic nitrogen compounds.

EXPERIMENTAL

2-Methyl- and 2 : 5-dimethyl-pyrazine were purified *via* the picrate from samples kindly donated by the Wyandott Chemicals Corporation. Tetramethylpyrazine was prepared by the reaction of ammonia with β-bromolævulic acid,[12] and 2 : 5-bis-(D-*arabo*tetrahydroxybutyl)-pyrazine from fructose and methanolic ammonia.[13] The specimen of 5-(D-*arabo*tetrahydroxybutyl)-2-methyl pyrazine, m. p. 202°, was isolated from the reaction products of invert sugar and ammonia (Davison and Wiggins, unpublished results). 3 : 6-Di*iso*butyl-2-hydroxypyrazine was kindly given by Professor F. S. Spring.

All measurements were carried out with a Radiometer type PO3h polarograph at 25 ± 0·5°. The capillary used had a value for $m^{2/3}t^{1/6}$ of 2·75 at the top of the first pyrazine wave in 0·5N-hydrochloric acid. Half-wave potentials were measured against a saturated calomel electrode by recording the polarograms manually with a mercury-pool anode and measuring the potential of the dropping-mercury electrode against a standard calomel electrode with a Cambridge pH meter. The gelatin solution used was freshly prepared each day.

Dissociation constants were measured with a Hilger Uvispec spectrophotometer. The spectra of the salt forms were measured in 2N-hydrochloric acid and of the free bases in water and dilute sodium hydroxide. The spectra when both forms were present were recorded in hydrochloric acid solutions of pH approximately equal to the pK_a of the pyrazine, except for tetramethylpyrazine when a 2mM-acetate buffer was used. The pH of the solutions was measured with a Cambridge pH meter. The pK_a values are not corrected for salt effects.

This work is sponsored by the British West Indies Sugar Research Scheme and the Sugar Research Foundation of the United States of America.

IMPERIAL COLLEGE OF TROPICAL AGRICULTURE,
TRINIDAD, B.W.I.

[*Received, June 25th,* 1956.]

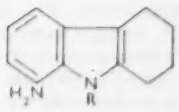
[9] Marshall and Walker, *J.*, 1951, 1004.
[10] Overend, Turton, and Wiggins, *J.*, 1950, 3505.
[11] Kolthoff and Lingane, "Polarography," Interscience, New York, 1952, p. 274.
[12] Wolff, *Ber.*, 1887, **20**, 428.
[13] de Bruyn and van Ekenstein, *Rec. Trav. chim.*, 1899, **18**, 76, 80.

933. *Experiments on the Preparation of Indolocarbazoles. Part IX.* The Preparation of 9-Methylindolo(2′ : 3′-1 : 2)carbazole.*

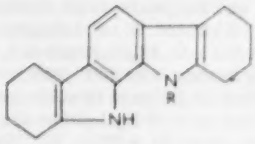
By R. J. Brunton, F. K. Drayson, (the late) S. G. P. Plant, and Muriel L. Tomlinson.

The preparation of 9-methylindolo(2′ : 3′-1 : 2)carbazole is described. It has been shown that Brown and Nelson's method of reducing nitro-compounds with hydrazine and Raney nickel is very suitable for the preparation of amino-tetrahydrocarbazoles.

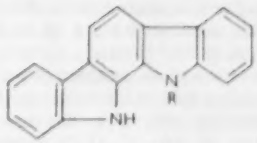
From 8-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (I; R = Me), 5 : 6 : 7 : 8 : 4′ : 5′ : 6′ : 7′-octahydro-9-methylindolo(2′ : 3′-1 : 2)carbazole (II; R = Me) has been prepared by condensation with 2-hydroxy*cyclo*hexanone; it has been successfully dehydrogenated to 9-methylindolo(2′ : 3′-1 : 2)carbazole (III; R = Me), the first derivative of the indolocarbazole (III; R = H) to be obtained. Derivatives of all but one, namely indolo(3′ : 2′-2 : 3)-carbazole (IV), of the five isomeric indolocarbazole systems, are therefore now known.[1,2,3,4]



(I)

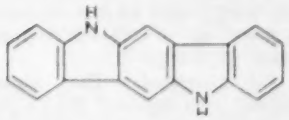


(II)

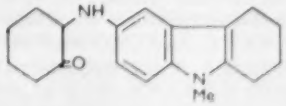


(III)

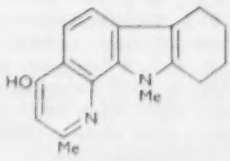
Attempts to prepare the parent substance (III; R = H) from 8-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (I; R = H) failed: reaction took place between this amine and 2-hydroxy*cyclo*hexanone, but no crystalline material could be obtained, even after dehydrogenation of the crude product. It does not appear that failure to obtain the indolocarbazole was caused by the 8-aminotetrahydrocarbazole reacting as an *ortho*-diamine and producing a phenazine derivative with 2-hydroxy*cyclo*hexanone [5] for no basic material could be extracted from the reaction mixture, and unlike *o*-phenylenediamine 8-aminotetrahydrocarbazole gives a diacetyl-compound, and not a glyoxaline, on prolonged boiling with acetic anhydride. It was not possible to acetylate 1 : 2 : 3 : 4-tetrahydro-8-nitrocarbazole, and so the possibility of preparing the parent indolocarbazole (III; R = H) from 9-acetyl-8-amino-1 : 2 : 3 : 4-tetrahydrocarbazole could not be explored.



(IV)



(V)



(VI)

Attempts to prepare indolocarbazoles from 6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole, from its 9-acetyl- and 9-methyl-derivative, and from 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole have all failed. In one case only was an intermediate, namely 1 : 2 : 3 : 4-tetrahydro-9-methyl-6-(2-oxo*cyclo*hexylamino)carbazole (V), obtained crystalline.

8-Amino-1 : 2 : 3 : 4-tetrahydrocarbazole and the corresponding 9-methyl derivative,

* Part VIII, *J.*, 1956, 1135.

[1] Clifton and Plant, *J.*, 1951, 461.
[2] Tomlinson, *J.*, 1953, 809.
[3] Hall and Plant, *J.*, 1953, 116.
[4] Swindells and Tomlinson, *J.*, 1956, 1135.
[5] Earle and Tomlinson, *J.*, 1956, 794.

6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole, and 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole have all been condensed with ethyl acetoacetate to form the corresponding ethyl β-(1 : 2 : 3 : 4-tetrahydrocarbazolylamino)crotonates, but only one pyridinocarbazole, namely 5 : 6 : 7 : 8-tetrahydro-4′-hydroxy-9 : 6′-dimethylpyridino(2′ : 3′-1 : 2)carbazole (VI), could be obtained by further loss of water.

Aminotetrahydrocarbazoles have previously been prepared by reduction of nitro-compounds with iron and hydrochloric acid;[6] zinc dust and aqueous alcoholic hydrogen chloride;[7] sodium hydrosulphite (dithionite) and alkali in alcohol;[3,9,10] and iron powder, alcohol, and a trace of hydrochloric acid;[8,10] but these substances, which are rather readily oxidised, are difficult to obtain pure and in quantity. It has now been found that Brown and Nelson's method[11] of reduction with hydrazine and Raney nickel in methanol solution will reduce tetrahydronitrocarbazoles to give good yields of the corresponding pure amines.

Experimental

9-Methylindolo(2′ : 3′-1 : 2)carbazole.—8-Amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (0·25 g.) was heated with 2-hydroxy*cyclo*hexanone (0·15 g.) and a trace of anilinium bromide. Frothing began at 120° and the temperature was raised to 150° for 5 min. The resulting glass crystallised in contact with ethanol, and the product was crystallised from acetic acid, forming greyish needles (0·1 g.) of *5 : 6 : 7 : 8 : 4′ : 5′ : 6′ : 7′-octahydro-9-methylindolo(2′ : 3′-1 : 2)carbazole*, m. p. 231° (Found : C, 81·8; H, 7·8. $C_{19}H_{22}N_2$ requires C, 82·0; H, 7·9%). Dehydrogenation of the crude product (0·5 g.) by heating it at 250—300° with palladium–charcoal (0·25 g.; containing 10% of Pd) under carbon dioxide, followed by sublimation *in vacuo* (210°/0·1 mm.) gave *9-methylindolo(2′ : 3′-1 : 2)carbazole* as prisms (0·1 g.) (from alcohol), m. p. 243—244° (Found : C, 84·4; H, 5·5. $C_{19}H_{14}N_2$ requires C, 84·4; H, 5·2%); $\lambda_{max.}$ 2100 (log ε 4·2243), 2590 (4·7180), 2730 (4·7161), 2880 (4·4321), 3260 (4·5208), 3490 (3·8353), 3645 (3·6862) Å. The indolocarbazole dissolved in sulphuric acid forming a red-brown solution, changed to olive-green, fading to brown on addition of a little nitric acid. *1 : 2 : 3 : 4-Tetrahydro-9-methyl-6-(2-oxocyclohexylamino)-carbazole* was prepared by heating equivalent quantities of 6-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole and 2-hydroxy*cyclo*hexanone at 125° for 5 min. It crystallised from ethanol as needles, m. p. 133° (Found : C, 76·8; H, 8·1. $C_{19}H_{24}ON_2$ requires C, 76·9; H, 8·1%).

Ethyl β-*(1 : 2 : 3 : 4-Tetrahydro-9-methylcarbazol-8-ylamino)crotonate.*—8-Amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (1·0 g.) was mixed to a paste with a little acetoacetic ester and treated with one drop of hydrochloric acid. Next day the solid was collected and *ethyl* β-*(1 : 2 : 3 : 4-tetrahydro-9-methylcarbazol-8-ylamino)crotonate* obtained as needles (1·1 g.), m. p. 135—136° (from alcohol) (Found : C, 72·8; H, 7·7. $C_{19}H_{24}O_2N_2$ requires C, 73·0; H, 7·7%). Prepared in a similar way, *ethyl* β-*(1 : 2 : 3 : 4-tetrahydrocarbazol-8-ylamino)crotonate* was obtained as prisms (0·8 g.), m. p. 133—134° (from ethanol) (Found : C, 72·5; H, 7·5. $C_{18}H_{22}O_2N_2$ requires C, 72·5; H, 7·4%), *ethyl* β-*(1 : 2 : 3 : 4-tetrahydrocarbozol-6-ylamino)crotonate* as needles (0·8 g.), m. p. 140—141° (from ethanol) (Found : C, 72·4; H, 7·3%), and *ethyl* β-*(8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazol-5-ylamino)crotonate* as prisms (1·2 g.), m. p. 149—150° (from ethanol) (Found : C, 64·8; H, 6·5. $C_{18}H_{21}O_2N_2Cl$ requires C, 65·0; H, 6·3%).

5 : 6 : 7 : 8-Tetrahydro-4′-hydroxy-9 : 6′-dimethylpyridino(2′ : 3′-1 : 2)carbazole.—The corresponding ethyl β-aminocrotonate (1·1 g.) was powdered and mixed with diphenyl (15 g.) and boiled under reflux for 10 min. Extraction with sodium hydroxide and subsequent acidification gave a solid which crystallised from aqueous alcohol to give *5 : 6 : 7 : 8-tetrahydro-4′-hydroxy-9 : 6′-dimethylpyridino(2′ : 3′-1 : 2)carbazole* (0·2 g.), m. p. 256—258° (decomp.) (Found : C, 71·5; H, 7·1. $C_{17}H_{18}ON_2,H_2O$ requires C, 71·6; H, 7·0%).

8-Amino-1 : 2 : 3 : 4-tetrahydrocarbazole.—Powdered 1 : 2 : 3 : 4-tetrahydro-8-nitrocarbazole (5 g.) and Raney nickel (2—3 g.) in methanol (250 c.c.) were heated under reflux and hydrazine (60% aqueous solution; 50 c.c.) mixed with methanol (100 c.c.) was added slowly during ½ hr. by which time the solution had become colourless. Nickel was removed by filtration and the solution was concentrated under slightly reduced pressure. Dilution with water then precipitated the amine, needles (2·5 g.) (from benzene), m. p. 162° (Edwards and Plant[7] give

[6] Perkin and Plant, *J.*, 1921, 1825.
[7] Edwards and Plant, *J.*, 1923, 2393.
[8] Fawcett and Robinson, *J.*, 1927, 2254.
[9] Perkin and Riley, *J.*, 1923, 2399.
[10] Robinson and Tomlinson, *J.*, 1934, 1524.
[11] Brown and Nelson, *J. Amer. Chem. Soc.*, 1954, **76**, 5149.

m. p. 159—160°) (Found: C, 77·1; H, 7·5. Calc. for $C_{13}H_{14}N_2$: C, 77·4; H, 7·5%). Boiled with acetic anhydride (1½ hr.) it gave *8-acetamido-9-acetyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, needles (from ethanol), m. p. 201—202° (Found: C, 71·2; H, 6·7. $C_{16}H_{18}O_2N_2$ requires C, 71·1; H, 6·7%). The following amines were prepared from the nitro-compound (5 g.) in a similar way: 6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (3·6 g.) m. p. 151—152° (from light petroleum); *8-amino*-1 : 2 : 3 : 4-*tetrahydro-9-methylcarbazole* (2·9 g.) (from aqueous ethanol), m. p. 116° after further recrystallisation from benzene (Found: C, 77·9; H, 7·9. $C_{13}H_{16}N_2$ requires C, 78·0; H, 8·0%); 6-amino-1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole (2·4 g.), m. p. 97—98° (from light petroleum) (Found: C, 77·9; H, 8·2. Calc. for $C_{13}H_{16}N_2$: C, 78·0; H, 8·0%); 6-amino-9-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazole, an oil, which gave, with acetic anhydride, *6-acetamido-9-ethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, m. p. 183—184° (from benzene) (Found: C, 75·1; H, 7·8. $C_{16}H_{20}ON_2$ requires C, 75·0; H, 7·8%); 9-acetyl-6-amino-1 : 2 : 3 : 4-tetrahydrocarbazole (1·6 g.), m. p. 138° (from light petroleum) (Robinson and Tomlinson gave m. p. 140°); and 5-amino-8-chloro-1 : 2 : 3 : 4-tetrahydrocarbazole (3·8 g.), decomp. at 160° without melting (from ethanol).

1 : 2 : 3 : 4-*Tetrahydro-9-methyl-8-nitrocarbazole*.—1 : 2 : 3 : 4-Tetrahydro-8-nitrocarbazole (5 g.) and powdered potassium hydroxide (7 g.) were boiled in acetone (100 c.c.) while dimethyl sulphate (7 c.c.) was slowly added during 1 hr. After it had been boiled for a further hour, the mixture was diluted with water and the precipitate was recrystallised from acetic acid from which 1 : 2 : 3 : 4-*tetrahydro-9-methyl-8-nitrocarbazole* (4·5 g.) separated as needles, m. p. 106° (Found: C, 67·7; H, 6·3. $C_{13}H_{14}O_2N_2$ requires C, 67·8; H, 6·1%). Alkylation of the corresponding 6-nitro-compound proceeded more readily: potassium hydroxide was used in concentrated aqueous solution and the reaction was complete in an hour. 1 : 2 : 3 : 4-Tetrahydro-6-nitrocarbazole (10 g.) afforded 1 : 2 : 3 : 4-tetrahydro-9-methyl-6-nitrocarbazole (9 g.), m. p. 183°, previously obtained by nitrating 1 : 2 : 3 : 4-tetrahydro-9-methylcarbazole, and 1 : 2 : 3 : 4-*tetrahydro-9-ethyl-6-nitrocarbazole* (7·2 g.) as yellow needles, m. p. 136°, from acetic acid (Found: C, 68·7; H, 6·5. $C_{14}H_{16}O_2N_2$ requires C, 68·8; H, 6·6%).

THE DYSON PERRINS LABORATORY,
OXFORD UNIVERSITY.

[*Received, July 23rd*, 1956.]

---

934. *Reactions of Organic Peroxides. Part VIII.** 1 : 3 : 3-*Trimethylindan-1-yl Hydroperoxide and its Conversion into* 2 : 4 : 4-*Trimethylchroman Derivatives.*

By WILLIAM WEBSTER and DONALD P. YOUNG.

1 : 1 : 3-Trimethylindane is readily oxidised to a hydroperoxide, the structure of which follows from its reduction to the known 1 : 3 : 3-trimethylindan-1-ol. In presence of acids, the hydroperoxide rearranges to give 2 : 4 : 4-trimethylchroman-2-ol and 2 : 4 : 4-trimethylchrom-2-en; the former compound has been synthesised. The hydroperoxide with ferrous sulphate in dilute aqueous ethanol gives 1-ethoxy-1 : 3 : 3-trimethylindane.

COMMERCIAL samples of di*iso*propylbenzene usually contain up to 10% of 1 : 1 : 3-trimethylindane,[1] which can be isolated from the mixture by distillation. Presumably it arises from cyclisation of *o*-di*iso*propylbenzene with loss of hydrogen.

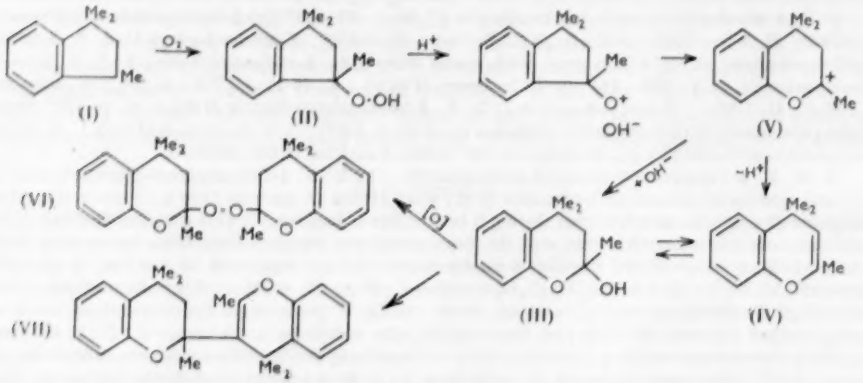
1 : 1 : 3-Trimethylindane (I) was readily converted by oxygen at 90°, in the presence of alkali, into a hydroperoxide. This hydroperoxide was not soluble in dilute sodium hydroxide but, on treatment of the oxidate with 40% sodium hydroxide solution, its sodium salt crystallised. The free hydroperoxide was regenerated from the salt by means of carbon dioxide, and was obtained as a solid, m. p. 38·5—40°; its structure as 1 : 3 : 3-trimethylindan-1-yl hydroperoxide (II) followed from its reduction to be known 1 : 3 : 3-trimethylindan-1-ol.[1]

When treated with a little fuller's earth or sulphuric acid in boiling acetone, trimethylindanyl hydroperoxide gave 2 : 4 : 4-trimethylchroman-2-ol (III) (40—50%) and its dehydration product, 2 : 4 : 4-trimethylchrom-2-en (IV) (25—40%). This is the first

* Part VII, *J.*, 1955, 3463.

[1] Colonge and Garnier, *Bull. Soc. chim. France*, 1948, 438.

recorded case where a hemiketal has been obtained directly from a hydroperoxide, although hemiketal esters have previously been obtained from hydroperoxide esters.[2] A ring-homologue of our hydroperoxide, 1 : 2 : 3 : 4-tetrahydro-1-methyl-1-naphthyl hydroperoxide, gives the expected keto-phenol.[3] The emergence of the cyclic hemiketal in the present case is attributed to its high stability. The amount of trimethylchromen (IV)



formed could not be accounted for by dehydration of the chromanol (III) under the reaction conditions, and the two products probably arose simultaneously from a common cationic intermediate (V).[4]

2 : 4 : 4-Trimethylchroman-2-ol (III) has previously been obtained [5] by decarbonylation of 2 : 4 : 4-trimethylchroman-1-carboxylic acid, the structure of which was established by synthesis. The m. p. of our product was in agreement with that previously recorded. To confirm its structure, it was synthesised by the method already used for its homologue.[5] 2 : 4 : 4-Trimethylchroman-2-carboxylic acid was converted into its amide, which was submitted to Hofmann rearrangement. Surprisingly, the product was not the expected trimethylchromanylamine but the chromanol (III) itself. Evidently the amine (which would be tautomeric with a phenolic ketimine) has an amino-group so labile that it was hydrolysed under the reaction conditions. Our proposed structure for the chromen (IV) rests on its relationship to the chromanol (III) ; the isomer with an exocyclic double bond is not excluded, but seems less likely.

2 : 4 : 4-Trimethylchroman-2-ol has also been reported [6] as arising from condensation of phenol and mesityl oxide in presence of sulphuric acid, but other workers [5,7] besides ourselves have been unable to repeat this preparation. The compound from the same reactants and hydrogen chloride, formerly regarded as (IV),[8] has recently been shown to be the isomeric 2 : 2 : 4-trimethylchrom-3-en ; [9] we had independently come to the same conclusion, since the compound was not identical with our chroman (IV) and had an ultraviolet absorption spectrum indicating that the double bond was conjugated with the aromatic ring.

Rearrangement of the hydroperoxide (II) in presence of " Indoil " alkanesulphonic acid (a mixture, approximately $C_4H_9{\cdot}SO_3H$) was accompanied by the formation of a

[1] Criegee and Zogel, *Chem. Ber.*, 1951, **84**, 215; Criegee, *Annalen*, 1948, **560**, 127; Wieland and Maier, *Ber.*, 1931, **64**, 1205.
[2] Hock, Depke, and Knauel, *Chem. Ber.*, 1950, **83**, 238.
[3] Cf. Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 748; Seubold and Vaughan, *J. Amer. Chem. Soc.*, 1953, **75**, 3790.
[4] Baker, Curtis, and McOmie, *J.*, 1952, 1774.
[5] Niederl, *J. Amer. Chem. Soc.*, 1929, **51**, 2426.
[6] Smith and Pritchard, *ibid.*, 1940, **62**, 771.
[7] Dianin, *J. Russ. Phys. Chem. Soc.*, 1914, **46**, 1310.
[8] Baker and McOmie, *Chem. and Ind.*, 1955, 256; Baker, Floyd, McOmie, Pope, Weaving, and Wild, *J.*, 1956, 2010.

by-product shown to be bis-2 : 4 : 4-trimethylchroman-2-yl peroxide (VI) by analysis. It appeared to have arisen by oxidation of the chromanol (III), and it was also obtained in small yield therefrom by use of hydrogen peroxide and a little sulphuric acid.

The trimethyl-chromanol (III) and -chromen (IV) had most of the usual properties of such compounds.[5,10] The chromen (IV) readily added water and alcohols in presence of acid to give the chromanol (III) and ethers thereof respectively, and these were easily split to regenerate the chromen. Dehydration of the chromanol in presence of sulphuric acid, however, gave considerable amounts of a dimer (VII). The chromen was only hydrogenated to trimethylchroman under comparatively drastic conditions, and it reacted with bromine by substitution rather than addition. Trimethylchromanol (III) did not show any of the normal properties of the tautomeric keto-phenol. Only by drastic treatment with an excess of concentrated sodium hydroxide solution and dimethyl sulphate was the methyl ether of the corresponding keto-phenol obtained.[11] Such stability is unusually high for an α-pyranol derivative, and may be connected with the heavy substitution on the heterocyclic ring. Chroman-2-ol, for example, readily yields a dinitrophenylhydrazone.[10] The action of dilute nitric acid on the chromanol (III) resulted in oxidative breakage of the pyran ring with simultaneous nitration of the benzene ring, the product being a (probably mixed) α-*o*-hydroxydinitrophenyl-α-methylpropionic acid.

The trimethylindanyl hydroperoxide reacted rather slowly with warm aqueous ferrous sulphate, and the product was almost entirely trimethylindene, evidently from dehydration of initially formed trimethylindanol. In dilute aqueous ethanol the reaction was much faster, and the major product was 1-ethoxy-1 : 3 : 3-trimethylindane. This ether was obtained for comparison by Williamson synthesis from trimethylindanol. The ether is presumably formed from the hydroperoxide (R·O·OH) by the attack of R·O· radicals on the ethanol. An etherification of ethanol in dilute aqueous solution must be unprecedented. Trimethylindanol was obtained here as a minor product, but only traces of ketonic material, apparently 3 : 3-dimethylindan-1-one and not *o-tert.*-butylacetophenone.

Experimental

No explosions or violent decompositions occurred during the preparation or handling of trimethylindanyl hydroperoxide, but the usual precautions were always observed. The hydroperoxide and its sodium salt are skin irritants.

" Light petroleum," unless otherwise stated, refers to the grade, b. p. 40—60°.

1 : 1 : 3-*Trimethylindane* (I).—Commercial di*iso*propylbenzene (Dow Chemical Co.) was fractionated through a 100-plate column. The intermediate cuts, b. p. 204—210°, between the *m*- and the *p*-di*iso*propylbenzene fractions from several distillations were combined and refractionated through a similar column, yielding fairly pure 1 : 1 : 3-trimethylindane, b. p. 204·8—204·9°/760 mm. (corr.), 81—84°/15 mm., n_D^{20} 1·5077 (Colonge and Garnier[1] give b. p. 90°/21 mm., n_D^{20} 1·5059). This contained 2—3% of other impurities detectable spectroscopically. The infrared spectrum showed a doubled band at 750 cm.$^{-1}$, and typical bands for an *ortho*-disubstituted benzene in the 1660—2000 cm.$^{-1}$ region; in the ultraviolet spectrum, the strongest band was at 2720 Å. These bands were not in agreement with any known dialkylbenzene or alkyltetralin, but were consistent with recorded data for indane and its homologues. Oxidation with chromium trioxide in acetic acid gave αα-dimethylhomophthalic acid, m. p. 121—122°, forming an anhydride, m. p. 80—81° (lit.,[1] 123° and 82·5—83° respectively).

1 : 1 : 3-*Trimethyl-x-nitroindane.*—Trimethylindane (20 ml.) was nitrated with fuming nitric acid (5 ml.) in acetic acid (20 ml.) and anhydride (14 ml.) at 30°, with cooling, affording a mixed mononitro-derivative (6 g.), b. p. 160—166°/18 mm. (Found : C, 70·6; H, 7·3; N, 6·4. Calc. for $C_{12}H_{15}O_2N$: C, 70·3; H, 7·4; N, 6·8%). This on dilution with methanol precipitated a solid of indefinite m. p., which after repeated recrystallisation from ethanol, methanol, and light petroleum gave a small amount of a sharp-melting *nitro-derivative*, m. p. 76—77° (Found : C, 70·1; H, 7·5; N, 6·8%). The infrared spectrum suggested that it was the 5- or 6-nitro-compound.

1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide* (II).—A mixture of 400 g. of trimethylindane

[10] Maitte, *Ann. Chim.* (*France*), 1954, **9**, 462.
[11] Cf. Baker, Curtis, and McOmie, ref. 5.

(93% pure) and 100 ml. of 2·5% aqueous sodium carbonate was stirred vigorously at 90° in a stream of oxygen. The rate of oxygen absorption at first accelerated to 10—11 mol.-% per hr., and then decreased slowly. Oxygenation was stopped after 8 hr., when 29 l. (N.T.P.) had been absorbed (52% calc. on hydrocarbon). The organic phase was diluted with 200 ml. of light petroleum; iodometric titration showed that it contained 1·15 equiv. (86% on oxygen absorbed) of hydroperoxide. The aqueous layer was rejected. A saturated solution of 70 g. of sodium hydroxide was added to the product with cooling and stirring. The sodium salt of the hydroperoxide crystallised, and after a few hours was collected, well washed with light petroleum, and decomposed by suspension in water and light petroleum and neutralisation with carbon dioxide. On concentration and strong cooling of the petroleum layer, the *hydroperoxide* crystallised in long fine needles, m. p. 38·5—40°, b. p. 70—71°/0·2 μ (Found: C, 74·7; H, 8·1%; iodometric equiv., 193. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·4%; equiv., 192).

The oxidation was also carried out with 400 g. of hydrocarbon and 5 g. of calcium hydroxide at 90°, with similar results.

Rearrangement of 1 : 3 : 3-*Trimethylindan*-1-*yl Hydroperoxide.*—(*a*) A solution of 100 g. of the hydroperoxide (II) (99% pure) in 200 ml. of acetone was added during 10 min. to a boiling solution of sulphuric acid (0·5 g.) in acetone (800 ml.). After boiling for a further 20 min., the solution contained very little hydroperoxide. It was neutralised by stirring with magnesium oxide (20 g.) for a few minutes, then separated, and the acetone driven off. The residue was dissolved in twice its weight of light petroleum. When this solution was cooled to −40°, 2 : 4 : 4-trimethylchroman-2-ol (III) crystallised; after recrystallisation it had m. p. 93·5—94° (Baker *et al.*[8] give 91°) (Found: C, 74·9; H, 8·2%; *M* in C_6H_6, 198. Calc. for $C_{12}H_{16}O_2$: C, 75·0; H, 8·4%; *M*, 192). The mother-liquors were freed from solvent and distilled through a short column into fractions as follows, analyses being by infrared spectroscopy:

B. p./mm.	Wt. (g.)	(IV) (%)	(III) (%)	Trimethylindene (%)	Trimethylindanol (%)
102—105°/16	7·27	60	1	10	—
105—122°/16	25·68	75	7	3	5
122—140°/16	9·36	15	40	—	—

The last fraction deposited some more solid trimethylchromanol (III). On the basis of the above analyses, the yields were (III) 48%, (IV) 28%. The indene and indanol could be accounted for by thermal decomposition of unrearranged hydroperoxide during distillation.

Refractionation of combined liquid products from several runs gave 2 : 4 : 4-*trimethylchrom*-2-*en* (IV), b. p. 104—106°/16 mm., n_D^{20} 1·5320, d_D^{20} 1·0049, $\lambda_{max.}$ 2850, 2775, and 2420 Å (ε 1500, 1670, and 4820 respectively) in *cyclo*hexane (Found: C, 83·0; H, 8·3. $C_{12}H_{14}O$ requires C, 82·8; H, 8·1%).

(*b*) A similar result obtained from the hydroperoxide (12 g.) with fuller's earth (No. 237, Fullers' Earth Union Ltd.; 2·0 g.) in boiling benzene (100 ml.) for 1·5 hr.

(*c*) The hydroperoxide (50 g.) with "mixed alkanesulfonic acid" (Indoil Chemical Co.; 4 ml.) in boiling acetone (400 ml.) yielded trimethylchromen (41%) and trimethylindene (7%). The solid product was a mixture of trimethylchromanol (28%), which was separated by leaching with hot ethanol, and *bis*-2 : 4 : 4-*trimethylchroman*-2-*yl peroxide*, m. p. 156° from ethyl acetate (Found: C, 75·4; H, 7·7%; *M* by peroxide estimation,[13] 378. $C_{24}H_{30}O_4$ requires C, 75·5; H, 7·9%; *M*, 382). This compound was also obtained (0·4 g. yield) from trimethylchromanol (III) (3·84 g.), 30% hydrogen peroxide (1·0 ml.), and sulphuric acid (1 drop) in ethanol (50 ml.), refluxed for 1 hr. and then set aside for 3 days.

Synthesis of 2 : 4 : 4-*Trimethylchroman*-2-*ol.*—2 : 4 : 4-Trimethylchroman-2-carboxylic acid [8] was converted into its *amide*, m. p. 140—142° (Found: C, 71·2; H, 8·0; N, 6·3. $C_{13}H_{17}O_2N$ requires C, 71·2; H, 7·8; N, 6·4%), which (7·1 g.) was subjected to the action of potassium hypobromite by the method used by Baker *et al.*[8] for its homologue. The product contained no acid-soluble material. The neutral organic product was leached with warm light petroleum, which left 0·85 g. of unchanged amide. The extract yielded 1·5 g. of trimethylchromanol, which after recrystallisation had m. p. 86—88°.

By omitting the dioxan solvent and any treatment with acid, a similar experiment yielded a solid product, m. p. 176—178°. This might have been bistrimethylchromanylurea (Found: N, 6·7. Calc. for $C_{25}H_{32}O_3N_2$: N, 6·9%), but no recognisable product was obtained from it hydrolysis.

[13] Dickey, Raley, Rust, Treseder, and Vaughan, *Ind. Eng. Chem.*, 1949, **41**, 1673.

Interconversion of **2 : 2 : 4-*Trimethylchroman*-2-*ol*** (III) ***and* 2 : 2 : 4-*Trimethylchrom*-2-*en*** (IV).—The chromanol (**50 g.**), benzene (**150 ml.**), and anhydrous oxalic acid (**1 g.**) were boiled in a Dean and Stark apparatus. The theoretical amount of water separated within 30 min. The undissolved oxalic acid was removed, and the solution was fractionated to give **43·2 g.** (96%) of **2 : 2 : 4**-trimethylchrom-2-en, b. p. **103—104°/15 mm.**, n_D^{20} **1·5320**, spectroscopically identical with the compound obtained from rearrangement of the hydroperoxide.

Catalysis with small amounts of sulphuric or phosphoric acid likewise gave quantitative yields of chromen, but dehydration in a similar manner of the chromanol (**30 g.**) over toluene-*p*-sulphonic acid (**0·5 g.**) gave **43%** of chromen and **36%** of **2 : 4 : 4-*trimethyl*-3-(2 : 4 : 4-*trimethylchroman*-2-*yl*)*chrom*-2-*en*** (VII), b. p. **156—164°/0·1 mm.**; this crystallised from ethanol in small flat needles, m. p. **70°** (Found : C, **82·5**; H, **8·2%**; *M* in C_6H_6, **346**. $C_{34}H_{38}O_2$ requires C, **82·8**; H, **8·1%**; *M* **352**). The infrared spectrum showed no functional groups but contained the chromen bands at **1230** and **1696 cm.$^{-1}$**, the latter (double bond) being reduced in intensity to half that in the chromen itself. This dimer (**2·6 g.**) with bromine in carbon tetrachloride at room temperature evolved hydrogen bromide and yielded a ***monobromo-derivative***, short needles (from light petroleum), m. p. **122°** (Found : C, **68·0**; H, **6·3**. $C_{34}H_{37}O_2Br$ requires C, **67·5**; H, **6·3%**). The dimer (**5 g.**) by oxidation with potassium permanganate in boiling acetone gave a little **2 : 4 : 4**-trimethylchroman-2-carboxylic acid (**0·05 g.**), m. p. **167—170°**, not depressed by an authentic sample.

The dimer was also obtained as a major product by dehydration of trimethylchromanol in presence of " Indoil " alkanesulphonic acid.

Trimethylchromanol was mainly unchanged when boiled in acetone containing **0·1%** sulphuric acid for **1 hr.**

Trimethylchromen (IV) (**10 g.**) and N-sulphuric acid (**100 ml.**) were refluxed for **3 hr.** The product was extracted with light petroleum, which on evaporation and cooling deposited **2·3 g.** (21%) of trimethylchromanol (III). The mother-liquor yielded **6·6 g.** of unchanged chromen. Doubling the reaction time gave the same amount of (III). When exposed to the atmosphere in the presence of a trace of sulphuric acid, the chromen changed within a few days into a crystalline mass of the chromanol (III).

2-Alkoxy*-2 : 4 : 4-*trimethylchromans*.**—**2 : 4 : 4**-Trimethylchroman-2-ol (III; **10 g.**) and N-hydrogen chloride in methanol (**100 ml.**) were boiled under reflux for **2·5 hr.** The methanol was distilled off, and the residue was taken up in light petroleum and washed free from acid, giving ***2-methoxy*-2 : 4 : 4-*trimethylchroman (**7·0 g.**), b. p. **121—124°/17 mm.**, n_D^{20} **1·5135**, d_4^{20} **1·0306** (Found : C, **75·7**; H, **8·5**; OMe, **14·2**. $C_{13}H_{18}O_2$ requires C, **75·6**; H, **8·8**; OMe, **15·0%**).

2 : 4 : 4-Trimethylchrom-2-en (IV; **10 g.**) similarly treated gave the same product (**8·8 g.**). The analogously prepared ***ethoxy-compound*** had b. p. **126°/15 mm.**, n_D^{20} **1·5039**, n_4^{20} **1·0028** (Found : C, **76·7**; H, **9·2**. $C_{14}H_{20}O_2$ requires C, **76·3**; H, **9·1%**). Although apparently pure it gave persistently low Zeisel ethoxyl values.

Distilling the methoxy- or ethoxy-trimethylchroman over a trace of sulphuric acid immediately regenerated trimethylchromen.

2 : 4 : 4-*Trimethylchroman*.—**2 : 4 : 4**-Trimethylchrom-2-en (IV) absorbed **1** mol. of hydrogen at **100—110°/700 lb./sq. in.** over Raney nickel. The product was the ***chroman***, b. p. **113·5°/16 mm.**, n_D^{20} **1·5219**, d_4^{20} **0·9921** (Found : C, **82·0**; H, **9·1**. $C_{13}H_{16}O$ requires C, **81·9**; H, **9·2%**). The chromen could not be hydrogenated over Adams catalyst at or below **50°**.

Bromination of **2 : 4 : 4-*Trimethylchrom*-2-*en*.**—Bromine (**9·2 g.**, **1** mol.) in carbon tetrachloride (**100 ml.**) was added to the chromen (**10 g.**). The bromine was immediately decolorised and hydrogen bromide was evolved. The solvent was removed under reduced pressure and the residue was distilled. The fraction, b. p. **100—105°/0·5 mm.**, n_D^{20} **1·5710** (**5·56 g.**), solidified. Recrystallised from aqueous ethanol, the ***3-bromo*-2 : 4 : 4-*trimethylchrom*-2-*en*** had m. p. **76—77°** (Found : C, **56·8**; H, **5·1**; Br, **32·0**. $C_{12}H_{13}OBr$ requires C, **57·0**; H, **5·2**; Br, **31·6%**). No bromide ion was formed by boiling methanolic sodium methoxide in **1·5 hr.**

The higher fractions, b. p. **>105°/0·1 mm.**, from this reaction contained more bromine than the monobromo-compound. This material (**15 g.**) was treated with bromine (**20 ml.**) without solvent for an hour, finally being warmed to **50°** to drive off hydrogen bromide and most of the excess of bromine. The residue was taken up in carbon tetrachloride, washed with **25%** sodium carbonate solution, and distilled. The product, ***3 : x : y : z-tetrabromo*-2 : 4 : 4-*trimethylchrom*-2-*en***, came over at **178—180°/0·2 mm.**, and, after recrystallisation from light petroleum (b. p. **60—80°**), had m. p. **120·5—122·5°** (Found : Br, **65·4**. $C_{13}H_{10}OBr_4$ requires Br, **65·1%**). This was likewise resistant to sodium methoxide.

Action of Nitric Acid on **2 : 4 : 4-*Trimethylchroman*-2-*ol*.**—A mixture of the chromanol

(20 g.), 70% nitric acid (100 ml.), and water (200 ml.) was warmed to 60°, whereupon a vigorous reaction took place which was moderated by cooling. After 30 min. the mixture was heated to the b. p. for 1 hr. Next morning the semisolid organic product was separated and leached with boiling benzene. The benzene solution was extracted with 2N-sodium hydroxide; acidification of this precipitated a solid which was recrystallised from toluene and then had m. p. 204—205° (decomp.). This was probably an *α-(2-hydroxy-x : y-dinitrophenyl)-α-methylpropionic acid* (Found : C, 44·8; H, 3·8; N, 10·0%; equiv., 137. $C_{10}H_{10}O_7N_2$ requires C, 44·5; H, 3·7; N, 10·4%; equiv., 135); the infrared spectrum was in accordance with this, but did not locate the nitro-groups.

Methylating Ring-fission of 2 : 4 : 4-Trimethylchroman-2-ol.—The chromanol (III) (0·4 g.) was boiled with sodium hydroxide (8 g.) in water (10 ml.) for 5 min., then cooled, and methanol (5 ml.) added, followed by methyl sulphate (5 ml.) slowly after 5 min.[11] The mixture was boiled for 15 min., cooled, diluted with water, and extracted with ether. The extract yielded an oil which was converted into the *2 : 4-dinitrophenylhydrazone*, m. p. 106—107° (from ethanol), of 4-*o*-methoxyphenyl-4-methylpentan-2-one (Found : C, 59·4; H, 5·2; N, 14·8. $C_{19}H_{22}O_5N_4$ requires C, 59·1; H, 5·7; N, 14·5%).

No reaction occurred when the chromanol (2 g.) was boiled with 2N-sodium hydroxide (20 ml.) and methyl iodide (1 ml.) for 2 hr.

Action of Sodium Sulphite on 1 : 3 : 3-Trimethylindan-1-yl Hydroperoxide.—(*a*) The hydroperoxide (98% pure; 19 g.) was stirred at 60° for 7 hr. with anhydrous sodium sulphite (100 g.) in water (300 ml.). The mixture was boiled for 3 hr. to complete the reaction. Extraction with benzene afforded 11·0 g. of 1 : 3 : 3-trimethylindan-1-ol, b. p. 66°/0·2 mm., m. p. 46—47°, which crystallised from light petroleum in fine needles (Colonge and Garnier [1] found m. p. 45°, b. p. 128°/25 mm.). The infrared spectrum was in accordance with their structure.

(*b*) The product from 71 g. of hydroperoxide (80% pure) was distilled at 14 mm., and proved to be mainly 1 : 1 : 3-trimethylindene, b. p. 98—105°/14 mm., leaving 10 g. of solid *bis-1 : 3 : 3-trimethylindan-1-yl peroxide*. This was slightly decomposed by recrystallisation from hot solvents, and was purified by dissolution in ether and reprecipitation with cold ethanol. It then had m. p. 77—79° (incomplete) (Found : C, 82·0; H, 8·3%; *M*, cryoscopic in C_6H_6, 334; by peroxide estimation,[12] 370. $C_{24}H_{30}O_2$ requires C, 82·4; H, 8·6%; *M*, 350). There was no detectable peroxide in the starting material.

Hydrogenation of 1 : 3 : 3-Trimethylindan-1-yl Hydroperoxide.—The hydroperoxide (82% pure; 30 g.) in methanol (30 ml.) was hydrogenated at room temperature and pressure over *ca.* 0·3 g. of 0·7% palladium-on-alumina. About 90% of the calculated quantity of hydrogen was absorbed in 3·5 hr. Evaporation of the filtered solution under reduced pressure left 26·7 g. of trimethylindanol.

Action of Ferrous Sulphate on 1 : 3 : 3-Trimethylindan-1-yl Hydroperoxide.—(*a*) The hydroperoxide (98% pure; 50 g.) in ethanol (200 ml.) was added in the course of 1·5 hr. to a solution of ferrous sulphate heptahydrate (168 g.) in water (400 ml.). The reaction was exothermic and was moderated by cooling; ferric hydroxide was precipitated. After a further 1·5 hours' stirring the organic product was extracted with benzene, washed, and distilled through an efficient column. The first fraction, b. p. 105—113°/16 mm. (5·3 g.), contained small amounts of a ketone, probably 3 : 3-dimethylindan-1-one (cf. next paragraph). It formed a scarlet *2 : 4-dinitrophenylhydrazone*, m. p. 256—257° (decomp.) (from benzene) (Found : N, 16·1. $C_{17}H_{16}O_4N_4$ requires N, 16·4%), and a semicarbazone, m. p. 209·5—210·5° (from water) (von Auwers [13] gives m. p. 205—207° for 3 : 3-dimethylindan-1-one semicarbazone). The main product was *1-ethoxy-1 : 3 : 3-trimethylindane*, b. p. 116—118°/16 mm. (17 g.) (Found : C, 82·9; H, 9·6. $C_{14}H_{20}O$ requires C, 82·5; H, 9·9%), n_D^{20} 1·5094, identified by comparison of its infrared spectrum with a synthetic sample (see below). The higher fractions, b. p. 120—121°/15 mm., were 1 : 3 : 3-trimethylindan-1-ol (12 g.).

(*b*) The hydroperoxide (33 g.) was stirred with ferrous sulphate heptahydrate (11 g.) in water (300 ml.) at 40° for 1 hr., and the mixture was then raised slowly to the b. p. Dilute sulphuric acid was added to the cooled mixture, and the organic product was collected in light petroleum, washed, and distilled. The main fraction, b. p. 88°/12 mm., n_D^{20} 1·5382, was 1 : 1 : 3-trimethylindene (19 g.). The higher fractions, b. p. 100—128°/12 mm. (3·2 g.), consisted by spectroscopic analysis of 25% of trimethylindene and 15—20% of trimethylindanol, besides some ketone. The last named was probably 3 : 3-dimethylindan-1-one again; it gave a dinitrophenylhydrazone, m. p. 275° (decomp.) (Found : C, 59·8; H, 4·7. $C_{17}H_{16}O_4N_4$ requires C, 59·9; H, 4·7%), and

[12] von Auwers, *Ber.*, 1921, **54**, 994.

semicarbazone, m. p. 212—214° (decomp.) (Found: C, 65·3; H, 7·0; N, 19·3. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·4%).

1 : 3 : 3-*Trimethylindene.*—1 : 3 : 3-Trimethylindan-1-ol (10 g.) in boiling benzene with toluene-*p*-sulphonic acid (1 g.) rapidly eliminated water, which was separated in a Dean and Stark trap. The washed solution yielded trimethylindene, b. p. 87·5°/15 mm., n_D^{20} 1·5370, d_4^{20} 0·9359 (Colonge and Garnier [1] record b. p. 94°/15 mm., n_D^{25} 1·5346, d_4^{22} 0·925).

1 : 3 : 3-*Trimethylindene Dimer.*—In an attempt to hydrate it, trimethylindene (30 g.) was boiled under reflux with sulphuric acid (54 g.) and water (30 ml.) for 4 hr. The product, isolated by dilution and extraction with light petroleum, was mainly unchanged olefin, but afforded 10·4 g. of the dimer, presumably 1 : 1 : 3-*trimethyl*-2-(1 : 3 : 3-*trimethylindan*-1-*yl*)*indene*, b. p. 181°/2 mm., n_D^{20} 1·5641 (Found: C, 91·0; H, 9·0. $C_{24}H_{28}$ requires C, 91·1; H, 8·9%). The ultraviolet absorption spectrum had $\lambda_{max.}$ 2920, 2620, and 2580 Å (ε 752, 6210, and 6210 respectively) in ethanol, indicating a conjugated double bond.

1-*Ethoxy*-1 : 3 : 3-*trimethylindane.*—Potassium (3·9 g.) was dissolved in a solution of 1 : 3 : 3-trimethylindan-1-ol (17·6 g.) in toluene (100 ml.), the mixture being boiled to complete the reaction. Ethyl iodide (30 g.) was then added, and the solution was boiled under reflux for 9 hr., a further 20 g. of ethyl iodide being added after 5 hr. The precipitated potassium iodide was washed out, after which the product was dried and fractionated. It contained much unchanged trimethylindanol, but the first fraction, b. p. 103—113°/18 mm., n_D^{20} 1·5108 (1·44 g.), consisted (by spectrographic analysis) of 80% of the ethyl ether, identical with the material described above.

Thanks are offered to Mr. B. Yeomans for practical assistance; to Mr. H. C. Highet for fractionating the starting material; to Messrs. A. R. Philpotts, W. Thain, W. R. Ward, and W. F. Maddams for recording and interpreting spectra; and to Mr. J. G. Maltby and his assistants for some analyses.

The Distillers Company Ltd., Research and Development Department, Great Burgh, Epsom, Surrey. [*Received, May 25th*, 1956.]

---

935. *Derivatives of Thionaphthen. Part II.* Thionaphthen Derivatives formed by Cyclisation of Acetonyl Aryl Sulphides and Aryl Phenacyl Sulphides.*

By J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton.

Cyclisation of phenacyl phenyl sulphide gives, not the expected 3-phenylthionaphthen, but 2-phenylthionaphthen (32% yield), whose structure has been proved by synthesis and degradation. 2-Phenylthionaphthen derivatives are similarly formed by the cyclisation of phenacyl *m*- and *p*-tolyl sulphides and 4-methoxyphenacyl phenyl sulphide. The compounds described [1] as 6-hydroxy- and 6-methoxy-3-phenylthionaphthen are now also found to be derivatives of 2-phenylthionaphthen. On the other hand, cyclisation of acetonyl phenyl sulphide is known to give 3-methylthionaphthen, without rearrangement. Various other substituted thionaphthens have been synthesised.

In early attempts to synthesise thionaphthen derivatives by the cyclodehydration of arylthio-ketones Delisle,[2] and Delisle and Schwalm,[3] used respectively acetonyl phenyl sulphide, $PhS{\cdot}CH_2{\cdot}COMe$, and ethyl (phenylthio)acetoacetate, $PhS{\cdot}CH(CO_2Et){\cdot}COMe$. Success was first achieved by Fries, Heering, Hemmecke, and Siebert [1] who cyclised *m*-hydroxyphenyl phenacyl sulphide and its methyl ether (I) with concentrated sulphuric acid to form what has hitherto been accepted as 6-hydroxy-3-phenylthionaphthen and its methyl ether (II). These two cyclisations, the only ones recorded until 1949, were doubtless aided by the

* Part I, Banfield, Davies, Ennis, Middleton, and Porter, *J.*, 1956, 2603.

[1] Fries, Heering, Hemmecke, and Siebert, *Annalen*, 1937, **527**, 110.
[2] Delisle, *Annalen*, 1890, **260**, 250.
[3] Delisle and Schwalm, *Ber.*, 1892, **25**, 2980.

activation of the position *para* to the strongly nucleophilic hydroxyl or methoxyl group, and do not justify the implication of a general synthesis given by Elderfield.[4] Such a general synthesis was begun [5] in 1948, by the preparation and attempted cyclisation of arylthio-ketones $ArS{\cdot}CH_2{\cdot}COR$ (R = aryl or occasionally methyl). This work was anticipated to a slight extent by Werner [6] who prepared ten arylthio-ketones, nine of which had the formula $Ar{\cdot}S{\cdot}CHR{\cdot}COMe$ (R = Me or H) and only one, $PhS{\cdot}CH_2{\cdot}COPh$, was of the phenacyl type. Werner, using phosphoric oxide or zinc chloride, successfully cyclised six of these to thionaphthen derivatives, all containing a 3-methyl substituent, but his efforts to cyclise phenacyl phenyl sulphide were unsuccessful.

The arylthio-ketones used were prepared by condensing 2-halogeno-ketones with arenethiols in the presence of base, but the process is more complicated than preparation of arylthioacetaldehyde acetals from the thiol and chloroacetaldehyde (Part I). First, when the ketone is phenacyl chloride and the base sodium hydroxide in ethanol, some of the phenacyl chloride is, despite the presence of the thiol, converted into "β-chlorodiphenacyl," [7] $C_{16}H_{13}O_2Cl$. Secondly, the 2-halogeno-ketones contain a positive halogen which can have an undesirable oxidising action on the thiol: thus, the interaction of phenacyl chloride and sodium *p*-tolyl sulphide in boiling methanol forms, not the desired sulphide, but acetophenone and phenacyl *p*-tolyl sulphoxide.[8] Similarly condensation of ethyl αα-dichloroacetoacetate and sodium thiophenoxide gave diphenyl disulphide and ethyl αβ-diacetylfumarate.[9] In the present work the oxidising effect in strong alkali of the positive halogen in phenacyl chloride has been repeatedly seen in the formation of large amounts of the diaryl disulphides.

Though these difficulties have been overcome with *p*-tolylthiomagnesium iodide in ether,[10] and by the rapid condensation at low temperatures of the very reactive phenacyl bromide with thiophenol in the presence of sodium methoxide,[11] it is now found that a very convenient condensing reagent for phenacyl chloride is boiling pyridine, the excess of which acts as solvent. It is particularly useful with *p*-acetamidothiophenol and other compounds containing groups sensitive to alkali.

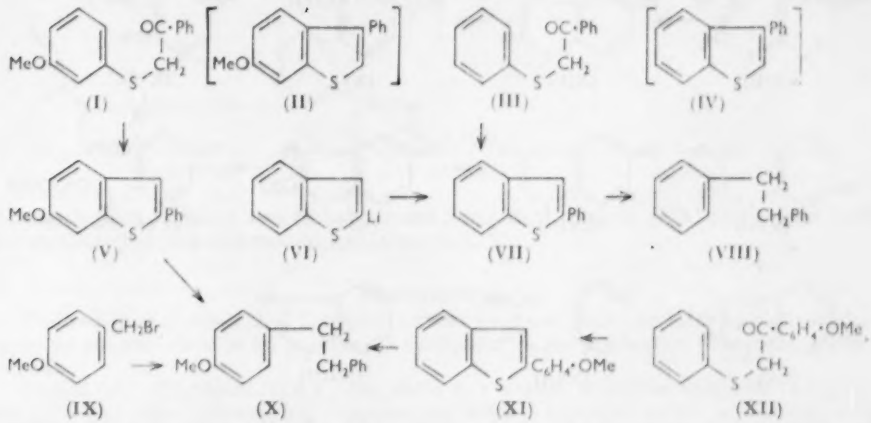
Arylthio-ketones are more resistant to acidic dehydrating agents than are arylthioacetaldehyde acetals, but like them readily suffer fission between the sulphur atom and the side chain, the original thiol or the disulphide from it being isolated. Oxalic acid is generally too weak a reagent, and concentrated sulphuric acid under ordinary conditions is too strong, though it is successful in cyclising 1-naphthyl phenacyl sulphide. It was independently found by some of the present workers and by Werner that phosphoric oxide and fused zinc chloride are often effective cyclising agents, but that they failed with phenacyl phenyl sulphide. However, this sulphide is cyclised (32% yield) by the prolonged use of polyphosphoric acid, which has so far been little used with compounds of this type. Many of the aryl phenacyl sulphides prepared resisted attempts to cyclise them with zinc chloride or phosphoric oxide, but polyphosphoric acid has not yet been tried with them.

The cyclisation of phenacyl phenyl sulphide (III) and some related compounds is now found to be subject to a rearrangement not previously observed in the synthesis of derivatives of thionaphthen. Polyphosphoric acid converts it in 32% yield into 2-phenylthionaphthen (VII), together with tar; 3-phenylthionaphthen (IV) has not been isolated from the product. Desulphurisation of the product (VII) with Raney nickel gives dibenzyl (VIII) (nitrated to 4 : 4'-dinitrodibenzyl, and oxidised to benzoic acid). Had 3-phenylthionaphthen (IV) been formed, desulphurisation would have given 1 : 1-diphenylethane, Ph_2CHMe, oxidation of which is known to yield benzophenone.[12] The 2-phenyl structure (VII) is further proved by synthesis of the compound from fluorobenzene and

[4] Elderfield, "Heterocyclic Compounds," Wiley, New York, 1950, Vol. II, p. 146.
[5] Banfield, Thesis, Melbourne, 1950.
[6] Werner, *Rec. Trav. chim.*, 1949, **68**, 509.
[7] Beilstein, "Handbuch der Organischen Chemie," Vol. XIX, p. 54.
[8] Kohler and Potter, *J. Amer. Chem. Soc.*, 1936, **58**, 2166.
[9] Otto and Rossing, *Ber.*, 1890, **23**, 756.
[10] Gilman and King, *J. Amer. Chem. Soc.*, 1925, **47**, 1136.
[11] Krollpfeiffer, Hartmann, and Schmidt, *Annalen*, 1949, **563**, 21.
[12] Beilstein, *op. cit.*, Vol. V, p. 60.

2-thionaphthenyl-lithium (VI), the constitution of the latter having been proved by its carboxylation to thionaphthen-2-carboxylic acid.[13]

A repetition of the cyclisation of *m*-methoxyphenyl phenacyl sulphide (I) with concentrated sulphuric acid by Fries *et al.*[1] gave a small amount of their product, m. p. 59°, but this compound is more easily obtained by the use of polyphosphoric acid. The product is desulphurised to give 4-methoxydibenzyl (X) identical with a specimen synthesised from 4-methoxybenzyl bromide and benzylmagnesium chloride. The cyclisation has therefore formed 6-methoxy-2-phenylthionaphthen (V) and not 6-methoxy-3-phenylthionaphthen



(II), desulphurisation of which would yield 1-*p*-methoxyphenyl-1-phenylethane. Had cyclisation occurred in the position *ortho* to methoxyl group, the resulting thionaphthen derivative would have yielded either 2-methoxydibenzyl or 1-*o*-methoxyphenyl-1-phenylethane on desulphurisation. Further, since demethylation of the compound, m. p. 59°, gave [1] the hydroxyphenylthionaphthen obtained by cyclisation of *m*-hydroxyphenyl phenacyl sulphide, it follows that the compound described by Fries [1] as 6-hydroxy-3-phenylthionaphthen is the 2-phenyl derivative.

Rearrangement also occurs in the cyclisation of 4-methoxyphenacyl phenyl sulphide (XII). The product must be 2-*p*-methoxyphenylthionaphthen (XI), for this also on desulphurisation gives 4-methoxydibenzyl (X).

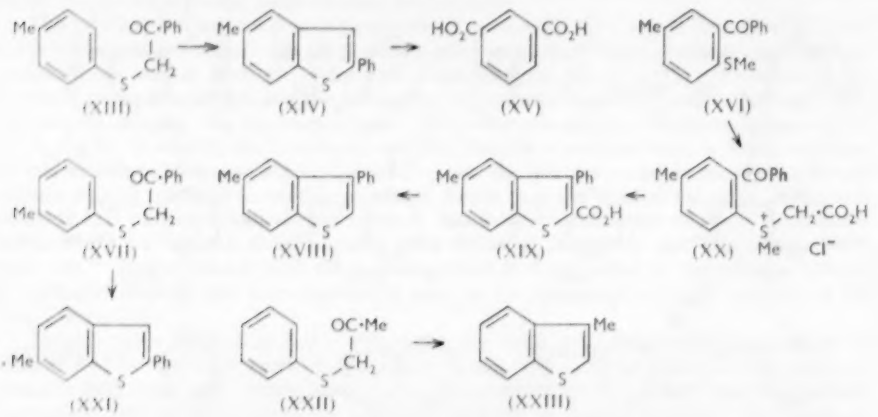
Similarly phenacyl *p*-tolyl sulphide (XIII) cyclises to form 5-methyl-2-phenylthionaphthen (XIV), desulphurisation of which gives a hydrocarbon (not characterised) considered to be 1-phenyl-2-*m*-tolylethane since it is oxidised to *iso*phthalic acid (XV) and benzoic acid; no *m*-benzoylbenzoic acid was obtained though this would be expected had the cyclisation product been 5-methyl-3-phenylthionaphthen (XVIII) whose derived hydrocarbon would be 1-phenyl-1-*m*-tolylethane. Now 5-methyl-3-phenylthionaphthen (XVIII) has been synthesised [14] by decarboxylation of 5-methyl-3-phenylthionaphthen-2-carboxylic acid (XIX) prepared unambiguously from 5-methyl-2-(methylthio)benzophenone (XVI). In confirmation of the structure (XVIII), it is now found that the oil obtained by this method yields *m*-benzoylbenzoic acid on desulphurisation and oxidation.

Four thionaphthen derivatives can theoretically be obtained by the cyclisation of phenacyl *m*-tolyl sulphide (XVII), where ring closure might occur *para* or *ortho* to the methyl group. 6-Methyl-2-phenylthionaphthen (XXI) should give 4-methyldibenzyl on reductive desulphurisation, and this would be oxidised to benzoic and terephthalic acid; these are indeed the only acids obtained from the homogeneous thionaphthen derivative formed in this cyclisation, and prove the structure (XXI).

[13] Shirley and Cameron, *J. Amer. Chem. Soc.*, 1950, **72**, 2788.
[14] Krollpfeiffer, Schneider, and Wissner, *Annalen*, 1950, **566**, 147.

Finally, the cyclisation of acetonyl phenyl sulphide (XXII) has been shown by Werner [6] to give 3- and not 2-methylthionaphthen, so that there is so far no evidence that rearrangement occurs in the cyclisation of ArS·CH_2·COR where R is alkyl.

It has been proved that rearrangement occurs with each of the five compounds Ar'S·CH_2·COAr examined. The yields are moderate (26—68%), and a considerable amount of tar is formed. Fries *et al.* cyclised the sulphide (I) in 55—60% yield, but the details in their paper are so vague that a repetition of their process by the present workers



has given only a minute yield of the product (V). In the cyclisation of arylthioacetaldehyde diethyl acetals (Part I), where there is no possibility of rearrangement, slight changes in conditions can cause much tar-formation and a great fall in yield. Hence it is felt that in the cyclisation of aryl phenacyl sulphides the moderate yield of the thionaphthen derivative is due to the imperfections of the process itself, rather than to the presence in the tar of much of the " normal " 3-arylthionaphthen derivative, of which so far none has been isolated. Probably the 3- are more easily fusible than the 2-arylthionaphthen derivatives [cf. the oily 5-methyl-3-phenylthionaphthen (XVIII) with 5-methyl-2-phenylthionaphthen (XIV), m. p. 158—158·5°], and this would render the isolation of the 3-aryl derivatives more difficult. Nevertheless, the present work indicates that the 2-aryl- are probably the main, if not the only, thionaphthen derivatives formed.

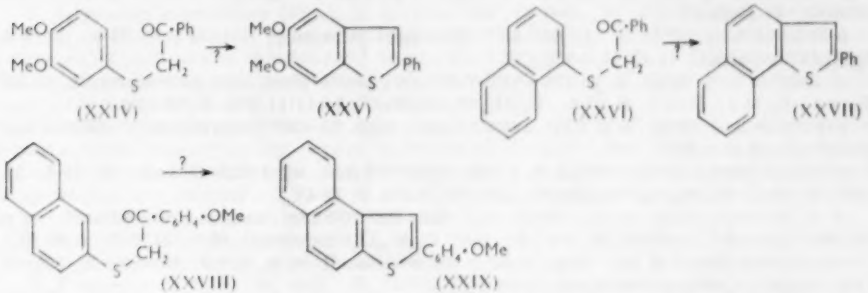
Our work leads to a tentative generalisation that in the cyclisation of ArS·CH_2·COR rearrangement occurs when R is a simple aryl and not when R is a simple alkyl group.

Accordingly the cyclisation products of acetonyl *o*- and *p*-tolyl sulphides are regarded as 3 : 7- and 3 : 5-dimethylthionaphthen respectively. Since Sunthankar and Tilak [15] have shown that the cyclisation of *m*-tolylthioacetaldehyde dimethyl acetal gives 6-methylthionaphthen, acetonyl *m*-tolyl sulphide should form 3 : 6-dimethylthionaphthen. It is remarkable that in the cyclisation of the three tolylthioacetaldehyde dimethyl acetals and the three acetonyl tolyl sulphides, the smallest yield of thionaphthen derivative is obtained from the *p*-tolyl type.

On the other hand, if rearrangement is assumed, the structures of a number of cyclisation products from various aryl phenacyl sulphide derivatives are considered definite for the following reasons. Since 3 : 4-dimethoxyphenylthioacetaldehyde diethyl acetal cyclises at a position *para* to one of the methoxyl groups (Part I), the product from 3 : 4-dimethoxyphenyl phenacyl sulphide (XXIV) should be 5 : 6-dimethoxy-2-phenylthionaphthen (XXV). By analogy, 5 : 6-dimethoxy-2-*p*-methoxyphenylthionaphthen should be the product from 3 : 4-dimethoxyphenyl 4-methoxyphenacyl sulphide. As cyclisation occurs in the 2- and not the *peri*-position with 1-naphthylthioacetaldehyde dimethyl and diethyl acetals (Part I)

[15] Sunthankar and Tilak, *Proc. Indian Acad. Sci.*, 1950, **32**, *A*, 396.

and with 3-1′-naphthylthiobutan-2-one,[6] it is likely that 1-naphthyl phenacyl sulphide (XXVI) would form 2-phenyl-6 : 7-benzothionaphthen (XXVII), and that 4-methoxyphenacyl 1-naphthyl sulphide would similarly give 2-*p*-methoxyphenyl-6 : 7-benzothionaphthen. Finally, 2-naphthylthioacetaldehyde diethyl acetal is known to cyclise in the



1-position (Part I), hence 4-methoxyphenacyl 2-naphthyl sulphide (XXVIII) should yield 2-*p*-methoxyphenyl-4 : 5-benzothionaphthen (XXIX).

Experimental

Preparation of Acetonyl Aryl Sulphides.—These have been made by using as condensation agent (a) aqueous alkali or (p) pyridine, as exemplified in the preparation of acetonyl phenyl sulphide.

Method (*a*). Thiophenol (11·0 g.) was added to a solution of sodium hydroxide (4·0 g.) in water (12·0 g.) under nitrogen, and bromoacetone (8·5 ml., 1·01 mol.) added, with stirring and ice-cooling, during ½ hr. After 2 hr. the mixture yielded to ether slightly impure acetonyl phenyl sulphide, m. p. 25—30°, b. p. 160—165°/22 mm. (8·8 g., 53%).

Method (*p*). Bromoacetone (5·0 ml., 1·31 mol.) was slowly added to a solution of thiophenol (5·0 g., 1 mol.) in pyridine (25 ml.), and after 5 min. the solution was heated on the water-bath for 10 min. The cooled solution, acidified with hydrochloric acid, yielded to ether acetonyl phenyl sulphide, m. p. 30—33°, b. p. 165—175°/28 mm. (4·8 g., 64%). Delisle [9] records m. p. 34—35°.

The following *acetonyl sulphides* were made essentially as above, though in method (a) a larger amount (about 1·2 mol.) of bromoacetone was used. The yields are calculated on the thiol. In the method (p) the reactants were sometimes kept at room temperature for many hours, but were not heated for more than ½ hr.

o-Tolyl (p, 3 days; 60%), b. p. 161—164°/22 mm., n_D^{16} 1·5750 (Found : C, 66·6; H, 6·7; S, 18·2. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·7; S, 17·8%).

m-Tolyl (p, 5 min.; 49%), b. p. 158—164°/19 mm., n_D^{18} 1·5674. Newell and Calaway [16] record b. p. 133—135°/7 mm.

p-Tolyl (purified through the bisulphite compound) (a, 55%; p, ¼ hr.; 58%), b. p. 164—168°/22 mm., n_D^{26} 1·5610. Delisle [9] records b. p. 150—157°/18 mm.

p-*Methoxyphenyl* (p, 5 min.; 55%), b. p. 180—182°/18 mm., n_D^{16} 1·5718 (Found : C, 61·6; H, 6·2; S, 16·8. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·1; S, 16·3%).

3 : 4-*Dimethoxyphenyl* (p, 1 hr.; 61%), b. p. 210—214°/28 mm., n_D^{16} 1·5778 (Found : C, 57·8; H, 6·3; S, 14·6. $C_{11}H_{14}O_2S$ requires C, 58·4; H, 6·2; S, 14·2%).

p-*Acetamidophenyl* (p, ½ hr., then heated for 1 min.; 68%), needles (from ethanol), m. p. 151° (Found : C, 59·05; H, 5·9; S, 14·4. $C_{11}H_{13}O_2NS$ requires C, 59·2; H, 5·8; S, 14·3%).

2-*Naphthyl* (a, 58%; p, 24 hr.; 96% yield of product, m. p. 37—40°, about 98% pure) (separated from a trace of non-volatile di-2-naphthyl disulphide, m. p. and mixed m. p. 138·5—139·5° by distillation with ethylene glycol at ordinary pressure), plates, m. p. 46—46·2° (from light petroleum) (Found : C, 72·3; H, 5·5; S, 14·5. $C_{12}H_{12}OS$ requires C, 72·2; H, 5·5; S, 14·8%).

1-*Naphthyl* (p, 12 hr.; 22%), b. p. 167—177°/0·4 mm. (Found : C, 72·5; H, 5·7; S, 14·5%).

[16] Newell and Calaway, *J. Amer. Chem. Soc.*, 1947, **69**, 116.

Preparation of Aryl Phenacyl Sulphides.—The thiol (1 mol.), usually dissolved in 1½—4 times its weight of pyridine, was refluxed with phenacyl chloride (1 mol.) for the time indicated. Similar heating is desirable to improve the low yields of some of the above acetonyl aryl sulphides, especially when derived from *o*-substituted thiols. The following *aryl phenacyl sulphides* were prepared : phenyl (6 hr.; 95%), b. p. 173—177°/0·5 mm., m. p. 52—53° (from ethanol); cf. Delisle.[8]

o-Tolyl (4 hr.; 50%), m. p. 65—66° (from light petroleum) (Found : C, 74·4; H, 5·8. $C_{15}H_{14}OS$ requires C, 74·4; H, 5·8%).

m-Tolyl (6 hr.; 72%), b. p. 176—182°/0·35 mm., plates (from light petroleum), m. p. 45° (Found : C, 74·1; H, 5·6; S, 13·5. $C_{15}H_{14}OS$ requires C, 74·4; H, 5·8; S, 13·2%).

p-Tolyl (4 hr.; 86%), b. p. 184—185°/0·1 mm., m. p. 35—36° (from ethanol). Gilman and King [10] record m. p. 37°.

p-*Methoxyphenyl* (9 hr.; 78%), b. p. 196—198°/0·2 mm., n_D^{16} 1·6229 (Found : C, 69·3; H, 5·45; S, 12·4. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·45; S, 12·4%).

3 : 4-*Dimethoxyphenyl* (5 hr.; 95%), b. p. 222—227°/0·5 mm., needles (from ethanol), m. p. 70—70·5 (Found : C, 66·75; H, 5·8; S, 11·0. $C_{16}H_{16}O_3S$ requires C, 66·7; H, 5·5; S, 11·2%).

p-*Acetamidophenyl* (½ hr.; 72%), needles (from ethanol), m. p. 121·5° (Found : N, 5·2; S, 11·6. $C_{16}H_{15}O_2NS$ requires N, 4·9; S, 11·2%).

2-*Naphthyl* (4 hr.; 66%), m. p. 96·5—97·5° (from ethanol) (Found : C, 77·9; H, 5·1; S, 12·0. $C_{18}H_{14}OS$ requires C, 77·7; H, 5·05; S, 11·5%).

1-*Naphthyl* (5 hr.; 74%), prisms (from ethanol), m. p. 83·5—84° (Found : C, 77·6; H, 5·15; S, 11·65%), of which the pale straw colour could not be removed by carbon.

m-Methoxyphenyl (6 hr.; 81%), m. p. 46—47°. Fries *et al.*[1] report m. p. 47°. The 2 : 4-*dinitrophenylhydrazone* recrystallised from alcohol in prisms, m. p. 153—154° (Found : N, 12·5. $C_{21}H_{18}O_5N_4S$ requires N, 12·8%).

The following were prepared without the use of pyridine.

p-Nitrophenyl phenacyl sulphide, identical with the product (m. p. 118°) of Waldron and Reid [17] who used sodium hydroxide, was obtained in 90% yield by using alcoholic ammonia (several hours at room temperature).

2 : 4-*Dinitrophenyl phenacyl sulphide* (good yield) began to separate in 1 min. after addition of phenacyl chloride to a warm solution of 2 : 4-dinitrothiophenol in alcoholic sodium hydroxide. Crystallised from ethanol, it had m. p. 170—171° (Found : C, 53·0; H, 3·45; N, 8·9. $C_{14}H_{10}O_5N_2S$ requires C, 52·8; H, 3·15; N, 8·8%).

The following aryl 4-*methoxyphenacyl sulphides* were prepared from 4-methoxyphenacyl chloride and the corresponding thiophenol in pyridine as described above :

Phenyl (4 hr.; 84%), plates (from ethanol), m. p. 89—90° (Found : C, 69·5; H, 5·5. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* formed needles (from alcohol), m. p. 169—170° (Found : N, 12·5. $C_{21}H_{18}O_5N_4S$ requires N, 12·8%).

3 : 4-*Dimethoxyphenyl* (4 hr.; 90%), needles, m. p. 46·5—47·5° (from ether–light petroleum) (Found : OMe, 29·25. $C_{17}H_{18}O_4S$ requires OMe, 29·3%). The p-*nitrophenylhydrazone* was orange plates (from ethanol), m. p. 164—165° (Found : C, 61·05; H, 5·4; N, 9·45. $C_{23}H_{22}O_5N_2S$ requires C, 60·9; H, 5·1; N, 9·3%).

1-*Naphthyl* (4 hr.; 68%), cream-coloured needles, m. p. 71° (from ethanol) (Found : OMe, 10·1. $C_{19}H_{16}O_2S$ requires OMe, 10·05%) [p-*nitrophenylhydrazone*, light yellow needles (from ethanol), m. p. 148·5° (Found : C, 68·0; H, 4·95; N, 9·55. $C_{25}H_{21}O_5N_3S$ requires C, 67·7; H, 4·75; N, 9·5%)].

2-*Naphthyl* (4 hr.; 95%), plates (from ether–light petroleum), m. p. 95·5° (Found : OMe, 10·2%) [p-*nitrophenylhydrazone*, light golden plates (from ethanol), m. p. 159—160° (Found : N, 9·4%)].

o-Tolyl (5 hr.; 85%), pale yellow prisms (from aqueous ethanol), m. p. 50° (Found : OMe, 11·5. $C_{16}H_{16}O_2S$ requires OMe, 11·4%) [p-*nitrophenylhydrazone*, golden-yellow plates (from ethanol), m. p. 162—163° (Found : N, 10·6. $C_{22}H_{21}O_5N_3S$ requires N, 10·3%)].

p-*Dimethylaminophenyl* (4 hr.; 70%), pale brown plates (from aqueous ethanol), m. p. 69—70° (Found : OMe, 10·1. $C_{17}H_{19}O_2NS$ requires OMe, 10·3%) [p-*nitrophenylhydrazone*, golden plates (from ethanol), m. p. 184—185° (Found : N, 12·85. $C_{23}H_{24}O_5N_4S$ requires N, 12·8%)].

Conversion of Acetonyl Aryl Sulphides into Thionaphthens.—3-Methylthionaphthen was readily prepared by Werner's method,[6] the action of phosphoric oxide at 160—190° or zinc chloride at 190° on acetonyl phenyl sulphide. However, appreciable amounts were recovered

[17] Waldron and Reid, *ibid.*, 1923, **45**, 240.

unchanged (25% after ¾ hour's heating with 0·33 part of phosphoric oxide at 160°, and 21% after ¾ hour's heating with 1½ parts of zinc chloride at 190°). The following were prepared.

3 : 7-*Dimethylthionaphthen* (60%), b. p. 122—124°/12 mm., m. p. 30—31°, n_D^{15} 1·6090, from equal weights of acetonyl *o*-tolyl sulphide and phosphoric oxide at 190° for ¾ hr. (Found : C, 74·1; H, 6·1; S, 19·6. $C_{10}H_{10}S$ requires C, 74·1; H, 6·2; S, 19·7%).

3 : 6-*Dimethylthionaphthen* (63%), b. p. 133—134°/18 mm., n_D^{15} 1·6158, from the *m*-tolyl sulphide similarly at 170° for 1½ hr. and then at 190° for ½ hr. (also, in 53% yield, from 1 part of ketone and 2 parts of zinc chloride for 7 hr. at 160—170°) (Found : S, 19·0%) [*picrate*, orange needles (from ethanol), m. p. 134·5—135·5° (Found : C, 49·1; H, 3·6; N, 11·2; S, 8·15. $C_{16}H_{12}O_7N_3S$ requires C, 49·1; H, 3·3; N, 10·75; S, 8·2%)].

3 : 5-Dimethylthionaphthen, b. p. 125—126°/14 mm., n_D^{15} 1·6010, in 27% yield from the *p*-tolyl sulphide similarly at 190° for ¾ hr. (a smaller yield was obtained by the use of equal parts of zinc chloride and the ketone at 170° for 40 min., then at 200° for 10 min., some thio-*p*-cresol being obtained also) (Found : C, 73·6; H, 6·2; S, 20·3%) [picrate, orange needles (from ethanol), m. p. 113—114° (from ethanol) (cf. ref. 11) (Found : N, 10·8%).

3-*Methyl*-6 : 7-*benzothionaphthen* (62%), m. p. 60·5—61·5°, b. p. 140—144°/0·3 mm., from the 1-naphthyl sulphide (1·4 g.) similarly at 190° for ¾ hr. (Found : C, 78·7; H, 5·1; S, 16·05. $C_{13}H_{10}S$ requires C, 78·8; H, 5·05; S, 16·1%) [*picrate*, orange prisms (from benzene–light petroleum), m. p. 125·5—127·5° (decomp.) (Found : S, 7·3; N, 10·1. $C_{19}H_{13}O_7N_3S$ requires S, 7·5; N, 9·85%)].

3-*Methyl*-4 : 5-*benzothionaphthen* (95%), m. p. 58·5—59·5°, b. p. 150—170°/0·5 mm. (accompanied by sublimation), from the 2-naphthyl sulphide with 4 times its weight of zinc chloride at 180° for ½ hr., then at 190° for ½ hr. (Found : C, 79·2; H, 5·2; S, 16·2%) [yellow *picrate* (from benzene–light petroleum), m. p. 152—153° (Found : S, 7·45; N, 10·1%)].

5 : 6-*Dimethoxy*-3-*methylthionaphthen* (83%), m. p. 107—107·5° (from light petroleum) from the 3 : 4-dimethoxyphenyl sulphide (5·6 g.) and phosphoric oxide (1·9 g.) at 170—175° for ½ hr. (the product was extracted with chloroform) (Found : C, 63·7; H, 5·95; S, 15·7; OMe, 29·6. $C_{11}H_{12}O_2S$ requires C, 63·5; H, 5·8; S, 15·4; OMe, 29·8%).

The *p*-methoxy- and *p*-acetamido-phenyl sulphides could not be cyclised with zinc chloride or with phosphoric oxide.

Cyclisation of Aryl Phenacyl Sulphides and their Derivatives.—In these cyclisations, times and temperatures are important.

(i) *Phenacyl phenyl sulphide.* The sulphide (5 g.), phosphoric oxide (35 g.), and phosphoric acid (20 ml.; *d* 1·75) were heated at 180—190° for 3 hr., and the cold mixture poured into water. Ether extracted 2-phenylthionaphthen (1·5 g., 32%), prisms, m. p. 175—176° (Found : C, 80·1; H, 4·8; S, 15·0. Calc. for $C_{14}H_{10}S$: C, 80·0; H, 4·8; S, 15·2%). Horton [18] gives m. p. 175·5—176°.

This product (0·8 g.) was refluxed with Raney nickel (8 g.) in ethylene glycol (30 ml.) for 8 hr., and the hot filtrate poured into water (250 ml.). The precipitate was washed twice with chloroform (75 ml.) and each washing was then used to extract the aqueous solution. The chloroform extract was dried ($MgSO_4$) and yielded a brown fragrant oil which was separated into two parts. One part was refluxed for 15 min. with water (10 ml.), powdered potassium permanganate (0·5 g.), and sodium carbonate (0·2 g.), the cold solution was clarified by sulphur dioxide, and benzoic acid separated (m. p. and mixed m. p. 120—121°). The second part was shaken with cold fuming nitric acid (2 ml.) for a few minutes, and the mixture was diluted with water, giving pale yellow prisms (from ethanol) of 4 : 4′-dinitrodibenzyl, m. p. 178—179°, mixed m. p. 179—180°.

A solution of thionaphthenyl-lithium was prepared by Shirley and Cameron's method [13] from *n*-butyl bromide (20 g.), lithium (2·45 g.), and thionaphthen (10 g.). To this solution was added freshly distilled fluorobenzene (6·3 g.) and after 24 hr. at room temperature, lithium fluoride separated. The mixture was poured into water (400 ml.), and the dried (Na_2SO_4) ethereal extract gave an oil from which excess of fluorobenzene and butyl bromide were removed under reduced pressure. The residual solid was fractionally crystallised from ethanol, to give prisms, m. p. and mixed m. p. 175—176°, of 2-phenylthionaphthen (8·6 g., 55% based on thionaphthen), and also needles (0·02 g., m. p. 260—262°) of (presumably) 2 : 2′-dithionaphthenyl which is recorded [13, 19] as having m. p. 262°.

(ii) *Phenacyl m-tolyl sulphide.* By the same procedure phenacyl *m*-tolyl sulphide and

[18] Horton, *J. Org. Chem.*, 1949, **14**, 761.
[19] Fries and Hemmecke, *Annalen*, 1929, **470**, 1.

polyphosphoric acid gave prisms (28%) (from ethanol), m. p. 184—184·5°, of *6-methyl-2-phenylthionaphthen* (Found: C, 80·4; H, 5·5; S, 14·0. $C_{15}H_{12}S$ requires C, 80·3; H, 5·35; S, 14·3%). Desulphurisation and oxidation as before gave two acids, the less soluble (in alcohol) of which was esterified to give dimethyl terephthalate, m. p. 138—139°, mixed m. p. 138—140°. The other acid was benzoic acid (m. p. and mixed m. p. 120—121°).

(iii) *Phenacyl p-tolyl sulphide.* With polyphosphoric acid as before, this sulphide afforded prisms (from ethanol), m. p. 158—158·5°, of *5-methyl-2-phenylthionaphthen* (26%) (Found: C, 80·3; H, 5·4; S, 14·1%). Desulphurisation and oxidation as before gave *iso*phthalic acid, needles (from ethanol), m. p. >300° (anilide, m. p. 246—248°, mixed m. p. 248—250°), and benzoic acid.

(iv) 5-Methyl-3-phenylthionaphthen, b. p. 155—157°/0·4 mm., was prepared by the method of Krollpfeiffer *et al.*,[14] who record b. p. 162°/1 mm. It was desulphurised and oxidised as was 2-phenylthionaphthen, giving needles (from ethanol), m. p. 161—162°; *m*-benzoylbenzoic acid has m. p. 162°.

(v) m-*Methoxyphenyl phenacyl sulphide.* With polyphosphoric acid (at 190° for 3 hr.) or cold concentrated sulphuric acid, this sulphide gave *6-methoxy-2-phenylthionaphthen*, prisms (from ethanol), m. p. 58—59° (not the 3-phenyl derivative as reported by Fries *et al.*,[1] who also report m. p. 59°).

The product (0·5 g.) was refluxed in absolute ethanol (150 ml.) with Raney nickel (8 g.) for ½ hr., the alcoholic solution filtered whilst hot, and the filtered metal washed with hot ethanol. The concentrated alcohol solution, after clarification (charcoal), yielded 4-methoxydibenzyl, m. p. 58—60° alone or mixed m. p. with an authentic specimen.

4-Methoxybenzyl bromide (from 4-methoxybenzyl alcohol; cf. Woodward[20] who used 3-methoxybenzyl alcohol) was treated with benzylmagnesium chloride as described by Späth,[21] affording 4-methoxydibenzyl, m. p. 60—61° (78%).

(vi) 3 : 4-*Dimethoxyphenyl phenacyl sulphide.* The sulphide with phosphoric oxide at 190° for ½ hr. gave (probably) *5 : 6-dimethoxy-2-phenylthionaphthen*, needles (from 80% ethanol), m. p. 116·5—117° (27%) (Found: C, 70·8; H, 5·1; S, 11·9; OMe, 23·2. $C_{16}H_{14}O_2S$ requires C, 71·2; H, 5·2; S, 11·9; OMe, 23·0%). The same product was obtained in 21% yield by the use of zinc chloride at 180° for ¾ hr.

(vii) 1-*Naphthyl phenacyl sulphide.* The sulphide (1 g.) was added gradually with stirring to cold concentrated sulphuric acid (15 ml.) and after 30 min. the deep red solution was poured on ice. The oil was extracted with light petroleum (b. p. 90—100°) in a continuous extractor for 2 hr. After removal of the petroleum the residual oil was dissolved in ether (50 ml.), light petroleum (50 ml.; b. p. 70—90°) added, and the mixture chromatographed on alumina. A broad yellow band (yellow fluorescence in ultraviolet light) was developed with ether, and its yellow eluate gave yellow needles, m. p. 50—56° (0·4 g.). Recrystallisation from ethanol or sublimation yielded yellow needles, m. p. 56—57°, regarded as *2-phenyl-6 : 7-benzothionaphthen* (Found: C, 82·8; H, 4·8; S, 12·3. $C_{18}H_{12}S$ requires C, 83·1; H, 4·6; S, 12·3%).

(viii) 4-*Methoxyphenacyl phenyl sulphide.* With polyphosphoric acid at 190° for 1 hr. this gave 2-p-*methoxyphenylthionaphthen*, prisms (from ethanol), m. p. 193—194° (44%) (Found: C, 75·1; H, 5·2. $C_{15}H_{12}OS$ requires C, 75·0; H, 5·0%), desulphurised as for the methoxy-compound in (V) above to 4-methoxydibenzyl, m. p. and mixed m. p. 59—61°.

(ix) 3 : 4-*Dimethoxyphenyl* 4-*methoxyphenacyl sulphide.* When heated with an equal weight of anhydrous zinc chloride at 175—180° for 40 min., the sulphide gave a black glass from which light petroleum (b. p. 30—90°) extracted a crystalline product which was recrystallised from light petroleum (b. p. 100—150°) to give colourless needles, m. p. 85—86°, regarded as 5 : 6-dimethoxy-2-*p*-methoxyphenylthionaphthen (53%). No picrate could be obtained from ethyl alcohol or benzene as solvent but it was obtained (red needles, m. p. 96—97°) by fusing equimolecular proportions of the compound and picric acid. Attempts to recrystallise this picrate resulted in its dissociation.

(x) 4-*Methoxyphenacyl* 1-*naphthyl sulphide.* Equal weights of this sulphide and zinc chloride were heated at 180° for 1 hr., the solid product powdered and boiled with water, and the aqueous suspension yielded to chloroform probably 2-p-*methoxyphenyl-6 : 7-benzothionaphthen* (64%), plates (from light petroleum), m. p. 164—165° (Found: OMe, 10·6. $C_{19}H_{14}OS$ requires OMe, 10·7%).

(xi) 4-*Methoxyphenacyl* 2-*naphthyl sulphide.* With zinc chloride at 170—175° for 1 hr. this

[20] Woodward, *J. Amer. Chem. Soc.*, 1940, **62**, 1481.
[21] Späth, *Monatsh.*, 1913, **34**, 2009

sulphide similarly gave pale brown needles, m. p. 157—158°, regarded as 2-p-*methoxyphenyl*-4 : 5-*benzothionaphthen* (68%) (Found : C, 78·9; H, 4·85; OMe, 10·6. $C_{19}H_{14}OS$ requires C, 78·6; N, 4·8; OMe, 10·7%). A picrate was obtained (m. p. 150—151°) as for 2-*p*-methoxyphenyl-5 : 6-benzothionaphthen above, but it also could not be recrystallised.

(xii) *Unsuccessful cyclisations.* Concentrated sulphuric acid at room temperatures and phosphoric oxide at 190° for ¼ hr., partly converted 2-naphthyl phenacyl sulphide into di-2-naphthyl disulphide (m. p. 139°). Anhydrous oxalic acid and stannic chloride were ineffective.

The following phenacyl sulphides could not be cyclised by the use of phosphoric oxide at 190° for 1 hr. : *o*-tolyl, *p*-acetamidophenyl, *p*-nitrophenyl, and 2 : 4-dinitrophenyl. Similarly, the following 4-methoxyphenacyl sulphides could not be cyclised by the use of sulphuric acid, stannic chloride, phosphoric oxide, or zinc chloride : *o*- and *p*-tolyl, *p*-acetamidophenyl.

The authors are indebted to the Dunlop Rubber Company of Australia Ltd. for research scholarships (to J. E. B. and N. W. G.). The microanalyses were carried out by Mr. N. L. Lottkowitz and by Dr. W. Zimmermann and his staff.

UNIVERSITY OF MELBOURNE, AUSTRALIA. [*Received, June 8th*, 1956.]

---

936. *Quantitative Microestimation of Formaldehyde in the Presence of Periodate and its Application to the Structural Examination of Carbohydrate Phenylosazones.*

By L. HOUGH, D. B. POWELL, and B. M. WOODS.

Colorimetric estimation of formaldehyde by means of phenylhydrazine and ferricyanide has been adapted for use in periodate oxidations.

A semimicro procedure for determining the positions of substituted groups in reducing monosaccharides has been devised by studying the periodate oxidation of phenylosazones of deoxy- and *O*-methyl-monosaccharides, and of disaccharides. Oxidations of unsubstituted hexose and pentose phenylosazones each yielded mesoxalaldehyde **1** : 2-bisphenylhydrazone and **1** mol. of formaldehyde. However, substitution of one of the hydroxyl groups in these phenylosazones resulted in the absence of one of these products.

A CONVENIENT method was required for studying the production of micro-quantities of formaldehyde during periodate oxidations of carbohydrates under varying conditions of pH. Schryver's method,[1] whereby formaldehyde is allowed to react with phenylhydrazine and ferricyanide reagents giving a mauve colour, has been improved by Dowse and Saunders,[2] but the use of this method for periodate studies demanded removal of all the periodate ion owing to interference with the colour reaction. The usual reagents for removal of periodate such as lead, arsenite, hydrogen sulphite, and stannous ions also interfered. Complete removal of periodate was effected by precipitation as the barium salt in the presence of sodium hydrogen carbonate, and subsequent estimations of formaldehyde were satisfactory.

Erythritol was used as a source of standard amounts of formaldehyde since periodate oxidations of erythritol in either unbuffered or buffered sodium hydrogen carbonate solution gave 2·0 mol. of formaldehyde as determined by the dimedone method,[3] and under both of these conditions the colorimetric method gave the same linear relation between erythritol concentration and intensity of colour. In agreement with Dowse and Saunders,[2] this direct relation was found to hold only over the range 1—45 μg. of formaldehyde. Oxidations of galactitol, D-mannitol, D-glucitol, D-glucose, and D-galactose in the presence of sodium hydrogen carbonate afforded theoretical quantities[4] of formaldehyde (±2%). Under unbuffered conditions, however, the hexitols gave low yields of formaldehyde

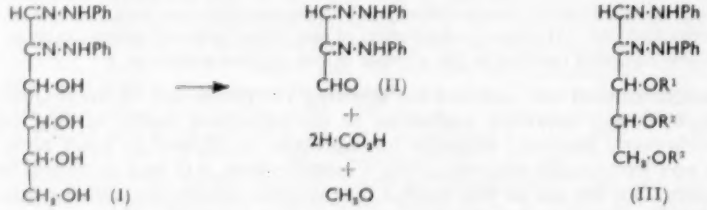
[1] Schryver, *Proc. Roy. Soc.*, 1910, *B*, **82**, 226.
[2] Dowse and Saunders, *Biochem. J.*, 1955, **60**, xxi.
[3] Bell, *J.*, 1948, 992.
[4] Reeves, *J. Amer. Chem. Soc.*, 1941, **63**, 1476.

(*ca.* 1·75 mol.), which was probably due to the presence of relatively stable formyl esters formed from the oxidation of intermediate cyclic hemiacetals.

Structural and enzymic studies of polysaccharides have necessitated the identification of disaccharide fragments, frequently in small yield, which are sometimes difficult to crystallise but often form crystalline phenylosazones. Purity of these phenylosazones can be determined for microquantities by paper chromatography [5] and by ultraviolet absorption data.[6] Periodate oxidations of various monosaccharide phenylosazones were studied for use as a semimicro procedure in subsequent investigations of the interglycosidic linkages present in phenylosazone derivatives of disaccharides.

In agreement with previous observations,[7] D-*arabino*hexose phenylosazone (cf. I) consumed the theoretical 3 mol. of periodate when oxidised in 50% alcohol at room temperature. No " over-oxidation " was observed because the cleavage product, mesoxalaldehyde 1 : 2-bisphenylhydrazone (II), was precipitated during the reaction. Simultaneously, 1 mol. of formaldehyde was formed, as determined by the colorimetric procedure, together with 2 mol. of formic acid.

Under the same conditions, D-*threo*pentose phenylosazone consumed 2·0 mol. of periodate with the formation of the product (II) and 0·9 mol. of formaldehyde. Oxidations of various deoxy- and *O*-methyl derivatives of monosaccharides (see Table) have shown that the production of the insoluble material (II) is characteristic for free hydroxyl groups at $C_{(3)}$ and $C_{(4)}$ of phenylosazone derivatives and that the liberation of formaldehyde requires the presence of a terminal glycol system. Similarly, phenylosazones derived from 1→4- and 1→3-linked dihexosaccharides (*e.g.*, maltose, cellobiose, lactose, and turanose) afforded 1 mol. of formaldehyde and none of insoluble material (II), whereas 1→6-linked dihexosaccharides (*e.g.*, melibiose) gave rise to the characteristic precipitate (II), but no formaldehyde. Thus, reaction under these conditions provides a quantitative method for differentiating between these two classes of dihexosaccharides, as little as 2 mg. of phenylosazone being required. Analogous results were obtained by Courtois, Wickstrom, and Le Dizet,[8] who estimated formaldehyde by the dimedone method, although their yields were not quantitative.



Maltose, cellobiose, and lactose phenylosazones rapidly consumed the theoretical 3 mol. of periodate (30 min.), which was followed by a slower over-oxidation, presumably involving the phenylhydrazone groups. The initial uptake of reagent could not be attributed entirely to glycol cleavage since triose phenylosazone consumed 1·3 mol. of periodate (constant value in 30 min.) and no formaldehyde or formic acid was detected. Likewise, the above workers [8] reported that glyoxal bisphenylhydrazone was also oxidised. Melibiose and turanose consumed 3 mol. of reagent rapidly, whereas the Malaprade theory requires that each should consume 4 mol. The reason for this behaviour is obscure, but it might perhaps be attributed to intramolecular interaction between the liberated reducing groups and the phenylhydrazone groups. In all cases, the disaccharide osazones gave less than theoretical yields of formic acid.

Application of the above procedure to disaccharides containing a pentose residue as the reducing group should provide a distinction between those which contain 1→5-, 1→4-,

[5] Barry and Mitchell, *J.*, 1954, 4020.
[6] Barry, McCormick, and Mitchell, *J.*, 1955, 222.
[7] Chargaff and Magasanik, *J. Amer. Chem. Soc.*, 1947, **69**, 1459.
[8] Courtois, Wickstrom, and Le Dizet, *Bull. Soc. chim. France*, 1952, 1006.

or 1→3-interglycosidic linkages. Periodate oxidation of the first (III; R^3 = glycosyl; $R^1 = R^2 = H$) would give rise to mesoxalaldehyde 1 : 2-bisphenylhydrazone (II), but not formaldehyde, whereas the last (III; R^1 = glycosyl; $R^2 = R^3 = H$) would yield formaldehyde but none of the hydrazone (II), whilst a 1→4-linked disaccharide (III; R^2 = glycosyl; $R^1 = R^3 = H$) would produce neither formaldehyde nor the hydrazone (II). Small quantities of 5-*O*-L-*arabino*furanosyl-L-arabinose and 3-*O*-L-*arabino*furanosyl-L-arabinose have been isolated [9] from the selective hydrolysis products of the araban component of sugar-beet pectin and this technique has been utilised in determining the interglycosidic linkages present in these disaccharides.

In all cases where periodate oxidation of a phenylosazone gave formaldehyde, the rate of formation was concomitant with the uptake of reagent and is consistent with the acyclic formulation suggested by Barry, McCormick, and Mitchell [6] and by Mester [10] for phenylosazones.

Experimental

Determination of Formaldehyde.—(i) *Reagent solutions.* "AnalaR" potassium ferricyanide was recrystallised from water, and then to a 2% aqueous solution concentrated hydrochloric acid (*d* 1·16) was added (2 : 5 v/v respectively).

"AnalaR" phenylhydrazine hydrochloride was dissolved in water (1 : 3 w/v respectively), and the solution was boiled for 30 min. with a little charcoal, filtered through a hot funnel, mixed with concentrated hydrochloric acid (1 : 3 v/v respectively), and cooled. The colourless crystals were collected, washed with acetone, and dried over phosphoric oxide under reduced pressure. A 1% solution of this purified material in 0·2N-sodium acetate–acetic acid buffer (pH 3·5) was prepared.

A saturated solution of barium chloride was added to a saturated solution of sodium hydrogen carbonate (4 : 1 v/v respectively), and the precipitate removed on the centrifuge. This reagent was prepared as required.

(ii) *Method.* The appropriate amount of polyhydroxy-compound (*e.g.*, 4·50 mg. of aldohexose) was dissolved in water (*ca.* 20 ml.), freshly prepared 0·3M-sodium metaperiodate solution (2 ml.) added, and the mixture made up to 25 ml. with water and stored in the dark at room temperature. At intervals, aliquot parts (2 ml.) were mixed with the barium chloride–sodium hydrogen carbonate reagent (2 ml.) contained in centrifuge tubes (10 ml.). [When barium chloride solution was used alone, periodate was not completely precipitated from solution. Oxidations carried out at pH >7·0 were buffered by the addition of saturated sodium hydrogen carbonate solution (2 ml.) and after withdrawal of aliquot parts (2 ml.) excess of periodate was removed by the addition of saturated barium chloride solution (2 ml.). During such oxidations [11] the pH rose from 7·85 to 8·75 in 24 hr.] After being kept for 10 min., the solutions were clarified on the centrifuge, aliquot parts (2 ml.) of the supernatant liquids were mixed with the phenylhydrazine reagent (2 ml.) and set aside in the dark for 30 min. Potassium ferricyanide reagent (7 ml.) was then added, and after 3 min. the mixture diluted with water to 50 ml. The clear solutions were thoroughly mixed and the absorptions at 518 mμ measured against a blank determination, either an "EEL" Portable Colorimeter (Filter No. 623) or a "Unicam" SP500 Photoelectric Absorptiometer being used. A calibration graph was constructed over the range 1—45 μg. of formaldehyde (from erythritol). Galactitol, D-mannitol, and D-glucitol gave after 3 hours' oxidation at room temperature under unbuffered conditions 1·76, 1·80, and 1·70 mol. of formaldehyde respectively, and in the presence of sodium hydrogen carbonate 1·96, 2·02, and 2·04 mol. of formaldehyde.

D-Galactose and D-glucose afforded 1·03 and 1·01 mol. of formaldehyde (constant values) respectively after oxidation for 35 min. in the presence of sodium hydrogen carbonate.

Phenylosazones.—These were prepared by Haskins, Hann, and Hudson's method; [12] the crude products were washed with benzene and recrystallised twice from ethanol–water. Each osazone gave a single zone when examined by chromatography [6] on Whatman No. 1 filter-paper circles, with toluene–ethanol–water (270 : 30 : 1 v/v) as mobile phase and ammoniacal silver nitrate as spray reagent. The molecular weights of the osazones were determined by Barry, McCormick and Mitchell's procedure [6] and were within ±2% of the theoretical values.

[9] Hough and Powell, unpublished results.
[10] Mester, *J. Amer. Chem. Soc.*, 1955, **77**, 4301.
[11] Personal communication from M. B. Perry, Queen's University, Canada.
[12] Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1946, **68**, 1766

Periodate Oxidation of Phenylosazones.—The osazone derivative (*ca.* 20 mg. accurately weighed) was dissolved in 50% ethanol (*ca.* 40 ml.), sometimes by heating and subsequent cooling, 0·3M-sodium metaperiodate (2 ml.) was added, and the whole made up to 50 ml. with 50% ethanol. After thorough mixing, the solution was stored in the dark and, at intervals, the periodate uptake and the liberated formic acid and formaldehyde were determined as follows. A blank containing no osazone was worked concurrently. The periodate uptake [13] was estimated on portions (5 ml.) which were transferred into a mixture of 0·2N-phosphate buffer (pH 7·0; 25 ml.) and 20% potassium iodide (2 ml.). Liberated iodine was titrated with 0·01N-sodium thiosulphate solution with 1% starch solution as indicator.

Phenylosazone of	Wt. (mg.)	Time (min.)	IO_4^- consumed (mol.)	$H{\cdot}CO_2H$ liberated (mol.)	CH_2O liberated (mol.)	1 : 2-Bisphenylhydrazone of mesoxalaldehyde [a]
D-Glucose	18·4	5	2·6	1·6	0·94	+
		15	2·9	1·7	1·01	
		160	3·0	1·9	1·01	
		1440	3·0	1·9	0·87	
3-*O*-Methyl-D-glucose	21·5	5	2·0	0·5	1·12	−
		15	2·2	0·6	1·15	
		160	2·3	0·8	1·08	
		1440	2·6	1·0	0·96	
D-Xylose	20·0	15	2·0	0·5	0·86	+
		60	2·0	0·6	0·91	
		120	2·0	0·6	0·89	
		1440	1·9	0·7	—	
Maltose	21·2	30	2·9	0·2	0·98	−
		240	3·5	0·3	0·94	
		360	3·7	0·6	0·95	
		1440	4·5	0·5	—	
Cellobiose	20·1	60	2·6	0·5	1·01	−
		180	3·0	0·6	1·01	
		300	3·2	0·6	0·93	
		1440	4·1	0·8	—	
Lactose	19·0	60	2·8	0·0	0·98	−
		180	3·4	0·3	1·17	
		480	3·7	0·6	1·09	
		1440	4·3	0·7	—	
Melibiose	22·0	30	2·8	0·6	0	+
		180	3·7	0·9	0	
		300	3·8	1·4	0	
		1440	4·6	1·0	0	
Turanose	21·6	30	2·8	0·6	1·00	−
		180	3·6	1·1	1·00	
		300	3·8	1·5	0·95	
		1440	4·7	0·9		
3-*O*-L-*arabino*Pyranosyl-L-arabinose	23·6	30	2·9	0·1	1·04	−
		180	3·6	0·3	1·06	
		360	3·9	0·5	1·06	
		1440	4·7	0·7	—	
3-*O*-α-D-*xylo*Pyranosyl-L-arabinose	3·0 [b]	30	—	—	1·02	−
		180	—	—	1·03	
		360	—	—	1·02	
		1400	—	—	0·88	
4-Deoxy-D-*erythro*hexulose	3·5 [b]	60	—	—	0·90	−
D-Glyceraldehyde	12·7 [c]	30	1·3	—	0	−
		120	1·3	—	0	
		180	1·3	—	0	

[a] M. p. and mixed m. p. 198° ± 1° and ultraviolet absorption identical with that of an authentic specimen. [b] In a total volume of 10 ml. [c] In a total volume of 25 ml.

Formic acid was determined in another sample (5 ml.), after addition of ethylene glycol (2 ml.), storage for 15 min., and dilution with 50% ethanol (5 ml.), by potentiometric titration to pH 8·2 with 0·01N-sodium hydroxide. The equivalence point was determined [14] by potentiometric titration of standard solutions of formic acid in 50% ethanol. Addition of 0·01N-formic

[13] Neumüller and Vasseur, *Arkiv Kemi*, 1953, **5**, 235.
[14] Anderson, Greenwood, and Hirst, *J.*, 1955, 225.

acid (5 ml.) to a solution of the phenylosazone of maltose in ethanol (5 ml.) followed by back-titration after 3 hr. with 0·01N-sodium hydroxide showed that the osazone did not consume any formic acid.

Formaldehyde determinations were carried out on samples (2 ml.) as described above, a calibration graph being obtained by oxidising erythritol in 50% ethanol. The results are given in the Table. When only small quantities of phenylosazone derivatives were available, any insoluble mesoxalaldehyde 1 : 2-bisphenylhydrazone produced in the oxidation mixtures was isolated for characterisation by separation on the centrifuge, and the supernatant liquors were used for formaldehyde determinations. The phenylhydrazone was thoroughly washed with water and recrystallised from aqueous ethanol.

Phenylosazones derived from 5-deoxy-L-arabinose, 5-deoxy-D-xylose, 5 : 6-dideoxy-D-*xylo*-hexose, L-rhamnose, and L-fucose gave mesoxalaldehyde 1 : 2-bisphenylhydrazone and no formaldehyde; L-*glycero*tetrose phenylosazone gave both formaldehyde and the hydrazone (II).

We thank Professor J. K. N. Jones and Dr. P. Andrews for specimens. One of us (B. M. W.) is grateful to the University of Bristol for the award of a Graduate Scholarship. As regards the second author (D. B. P.), this work forms part of the programme of the Food Investigation Organisation of the Department of Scientific and Industrial Research.

THE UNIVERSITY, BRISTOL. [*Received, July 23rd*, 1956.]

---

937. *Aryldihydroresorcinols. Part II.* The Influence of the Nitro-group in Dihydro-5-o-nitrostyrylresorcinol.*

By E. E. AYLING and D. A. DAVIES.

Dihydro-5-styrylresorcinol resembles an alkyl- rather than an aryl-dihydroresorcinol.

The influence of the nitro-group in dihydro-5-*o*-nitrostyrylresorcinol is much less marked than that in dihydronitrophenylresorcinols, the nitrostyryl being comparable with the styryl and the phenyl compound but a little less reactive.

DIHYDRO-5-STYRYLRESORCINOL behaves as a typical dihydroresorcinol in its reactions with phosphorus halides. With phosphorus trichloride and tribromide 3-chloro- and 3-bromo-5-styryl*cyclo*hex-2-en-1-one respectively are obtained, in yields comparable with but slightly less than those of the corresponding halogeno-ketones given by dihydrophenylresorcinol.[1,2] With two molecular proportions of phosphorus pentachloride the dihydroresorcinol yields 1 : 3-dichloro-5-styryl*cyclo*hexa-1 : 3-diene and with four molecular proportions 3 : 5-dichlorostilbene. Dihydrostyrylresorcinol appears to be somewhat more reactive towards phosphorus pentachloride than is dihydrophenylresorcinol [3] but not quite so reactive as dihydrodimethylresorcinol,[4] the respective yields of the corresponding dichloro*cyclo*hexadienes being 79, 62, and 85%. With phosphorus pentabromide only a tribromo-derivative could be isolated, apparently 2-bromo-5-αβ-dibromophenethyldihydroresorcinol, the formation of which is probably due to the tendency of phosphorus pentabromide to behave as a mixture of bromine and phosphorus tribromide in this type of reaction,[5] the 2-position and the ethylene bond being attacked.

With bromine, dihydrostyrylresorcinol behaves as an alkyl- rather than as an aryl-dihydroresorcinol since it yields 2 : 2-dibromo-5-αβ-dibromophenethyldihydroresorcinol, thus resembling dihydrodimethylresorcinol (which gives the 2 : 2-dibromo-derivative),[6] rather than dihydrophenylresorcinol (which only gives the 2-bromo-derivative [1]).

* Part I, *J.*, 1956, 2679.

[1] Boyd, Clifford, and Probert, *J.*, 1920, **117**, 1383.
[2] Hinkel and Hey, *J.*, 1928, 1202.
[3] Hinkel and Hey, *J.*, 1928, 2789.
[4] Crossley and Le Sueur, *J.*, 1902, **81**, 826.
[5] Crossley and Le Sueur, *J.*, 1903, **83**, 113.
[6] Vorländer and Kohlmann, *Annalen*, 1902, **322**, 257.

Whilst dihydronitrophenylresorcinols differ considerably from dihydrophenylresorcinol in their reactions with phosphorus chlorides,[7] the influence of the nitro-group in dihydro-5-*o*-nitrostyrylresorcinol is much less marked. The dihydroresorcinol yields 3-chloro- and 3-bromo-5-*o*-nitrostyryl*cyclo*hex-2-en-1-one with the appropriate phosphorus trihalide, although in slightly smaller yield than is obtained from the styryl compound. With either two or four molecular proportions of phosphorus pentachloride the only product isolated was 3 : 5-dichloro-2'-nitrostilbene. This was unexpected and was probably due to an easy conversion of the expected dichloro*cyclo*hexadiene into the stilbene derivative under these conditions.[8] An excess of bromine yielded only a dibromo-derivative, with no apparent addition at the ethylenic bond of the nitrostyryl group, probably owing to a deactivating influence of the nitro-group.

The reactivity of 5-aryldihydroresorcinols has been correlated [7] with the electron affinity of the aryl group (cf. also Part I) and the resemblance of the styryl compound to an alkyl rather than an aryl compound would be expected, the relative affinities of the phenyl, styryl, and methyl groups being indicated by the strengths of the acids : benzoic, cinnamic, and acetic acids, 10^5K 6·27, 3·65, and 1·75 respectively.[9] With dihydro-5-*o*-nitrostyrylresorcinol, the electron affinity of the nitrophenyl group should not be transmitted through the ethylenic bond to any marked extent but the electron-donating properties of the aralkyl group would be weakened, and the strength [9] of *o*-nitrocinnamic acid (10^5K 7·07) indicates that the dihydroresorcinol should resemble, but be somewhat less reactive than, the phenyl compound.

Dihydro-5-*o*-nitrostyrylresorcinol was only obtained in poor yield from 6-*o*-nitrophenylhexa-3 : 5-dien-2-one, considerable polymerisation still occurring even when ether was substituted for ethanol or benzene as the reaction medium. It was more satisfactory to isolate and then hydrolyse the ethyl dihydronitrostyrylresorcylate rather than to hydrolyse the ester without isolating it.[10] Alternative routes *via* diethyl *o*-nitrocinnamylidenemalonate or β-(*o*-nitrostyryl)acrylic acid were even less fruitful.

Experimental

Action of Phosphorus Trichloride on Dihydro-5-styrylresorcinol.—Dihydrostyrylresorcinol [11] (5 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus trichloride (1·6 g., 1 mol.) for 3 hr. The chloroform was evaporated and crushed ice added to the residue, the mixture then being extracted with ether. The extract was washed with 4% sodium hydroxide solution and water, and dried (Na_2SO_4). Evaporation of the ether yielded 3-*chloro*-5-*styryl*cyclo*hex*-2-*en*-1-*one* (3·2 g., 59%) as a pale yellow oil, which solidified when frozen, and crystallised from aqueous methanol as a microcrystalline powder, m. p. 44° (Found : Cl, 15·1. $C_{14}H_{13}OCl$ requires Cl, 15·2%).

Action of Phosphorus Pentachloride on Dihydro-5-styrylresorcinol.—(*a*) The dihydroresorcinol (10 g., 1 mol.) was suspended in dry chloroform (25 c.c.), phosphorus pentachloride (19·5 g., 2 mol.) added in small quantities, and the mixture heated under reflux for 3 hr. The above procedure gave 1 : 3-*dichloro*-5-*styryl*cyclo*hexa*-1 : 3-*diene* (9·3 g., 79%), b. p. 140°/0·23 mm., which solidified and crystallised from aqueous ethanol in plates, m. p. 83° (Found : C, 67·5; H, 5·0. $C_{14}H_{12}Cl_2$ requires C, 67·0; H, 4·8%).

(*b*) The dihydroresorcinol (5 g., 1 mol.) was suspended in dry chloroform (15 c.c.), phosphorus pentachloride (19·5 g., 4 mol.) gradually added, and the mixture heated on a water-bath for 3 hr. Subsequent procedure as above yielded 3 : 5-*dichlorostilbene* as a reddish-yellow oil (5 g., 86%), b. p. 164—166°/0·7 mm., which solidified when frozen and crystallised from aqueous methanol in short needles, m. p. 80°, depressed by ~25° when mixed with the above dichlorostyryl*cyclo*hexadiene (Found : C, 67·6; H, 4·3. $C_{14}H_{10}Cl_2$ requires C, 67·5; H, 4·0%).

Action of Phosphorus Tribromide on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (5 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus tribromide (3·1 g.,

[7] Hinkel and Dippy, *J.*, 1930, 1387.
[8] Crossley and Le Sueur, *J.*, 1902, **81**, 1534.
[9] Dippy, *Chem. Rev.*, 1939, **25**, 206.
[10] Crossley and Pratt, *J.*, 1915, **107**, 173.
[11] Vorländer and Erig, *Annalen*, 1897, **294**, 312.

1 mol.) for 3 hr. The above procedure gave *3-bromo-5-styrylcyclohex-2-en-1-one* (3·5 g., 54%) which solidified and crystallised from aqueous ethanol in white needles, m. p. 69° (Found: C, 60·4; H, 4·8; Br, 28·9. $C_{14}H_{13}OBr$ requires C, 60·7; H, 4·7; Br, 28·8%).

Action of Phosphorus Pentabromide on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (5 g., 1 mol.) was suspended in dry chloroform (15 c.c.), and phosphorus pentabromide (20·1 g., 2 mol.) added in small quantities. The mixture was heated for 3 hr. and, by following the usual procedure, a red oil (7·25 g.) was obtained. Cooling and addition of ether yielded a pink solid (2·9 g.), which was dissolved in methanol, treated with charcoal, heated to boiling, and then filtered. Addition of water to the filtrate precipitated *2-bromo-5-αβ-dibromophenethyldihydroresorcinol* as a white solid which, crystallised from ethanol, had m. p. 155° (Found: C, 37·0; H, 2·8. $C_{14}H_{12}O_2Br_3$ requires C, 37·1; H, 2·9%). The ether solution yielded a red oil which decomposed when distillation under reduced pressure was attempted.

Action of Bromine on Dihydro-5-styrylresorcinol.—Bromine (2·8 g., >3 mol.) in dry chloroform (24 c.c.) was added during 1 hr. to a suspension of the dihydroresorcinol (1·07 g., 1 mol.) in chloroform (15 c.c.). Next day the suspended solid was filtered off and dried in a vacuum-desiccator over sodium hydroxide. Crystallisation from aqueous acetone yielded 2 : 2-*dibromo-5-αβ-dibromophenethyldihydroresorcinol*, m. p. 185° (decomp.) (Found: Br, 59·2. $C_{14}H_{12}O_2Br_4$ requires Br, 60·1%).

Treatment of the dihydroresorcinol (1 mol.) with bromine (1 or 2 mol.) as above yielded only mixtures from which no pure compound could be isolated.

Action of 2 : 4-Dinitrophenylhydrazine on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (0·54 g., 1 mol.) and 2 : 4-dinitrophenylhydrazine (0·92 g., 2 mol.) were heated to boiling in ethanol (50 c.c.). The solution was cooled slightly, concentrated hydrochloric acid (1 c.c.) added, and the solution heated under reflux for 2·5 hr. During the heating *dihydrostyrylresorcinol·bis-2 : 4-dinitrophenylhydrazone trihydrate* separated as a yellow solid, m. p. 188° (1·36 g., 87%) (Found: C, 50·4; H, 4·2; N, 17·3. $C_{26}H_{22}O_8N_8,3H_2O$ requires C, 49·7; H, 4·5; N, 17·8%). Crystallisation from aqueous acetone gave the *monohydrate* as a dark purple solid, m. p. 228°, the change in colour suggesting such a loss of water of crystallisation (Found: C, 53·3; H, 3·9; N, 18·5. $C_{26}H_{22}O_8N_8,H_2O$ requires C, 52·7; H, 4·1; N, 18·9%).

6-o-*Nitrophenylhexa-3 : 5-dien-2-one.*—A mixture of *o*-nitrocinnamaldehyde (10 g.), acetone (30 c.c., excess), water (200 c.c.) and 10% aqueous sodium hydroxide (8 c.c.) was shaken for 24 hr. at room temperature. 6-*o*-Nitrophenylhexa-3 : 5-dien-2-one separated as a brown solid which crystallised from light petroleum (b. p. 80—100°) in pale yellow needles, m. p. 73·5° (9·1 g., 74%). Diehl and Einhorn [12] record m. p. 73·5°.

Ethyl Dihydro-5-o-nitrostyrylresorcinol-4-carboxylate.—Sodium (2 g., 1 g.-atom) was dissolved rapidly in ethanol, excess of which was then removed under reduced pressure, and to the resulting sodium ethoxide was added ethyl malonate (17 c.c., >1 mol.). As soon as the sodium ethoxide had reacted with the ester, ether was added, a finely divided precipitate of ethyl sodiomalonate being obtained. 6-*o*-Nitrophenylhexa-3 : 5-dien-2-one (19·0 g., 1 mol.) was then added gradually with shaking and the mixture heated under reflux for 48 hr. The sodium salt of the dihydroresorcylic ester, which separated during the condensation, was filtered off and dissolved in water, the solution then being shaken with ether until the ether ceased to be coloured yellow. The aqueous solution was acidified and the liquid decanted from the light brown oil which separated. Trituration of this oil with ethyl acetate gave *ethyl dihydro-5-o-nitrostyrylresorcinol-4-carboxylate* as a light brown solid, which crystallised from aqueous ethanol as a pale yellow powder, m. p. 144° (6·4 g., 22%) (Found: C, 61·8; H, 5·0. $C_{17}H_{17}O_6N$ requires C, 61·6; H, 5·2%).

When ethanol or benzene (cf. Part I) was employed as the reaction medium polymerisation of the unsaturated ketone occurred, and no dihydroresorcylic ester could be isolated. A similar result was obtained when toluene, anisole, dioxan, or light petroleum (b. p. 80—100°) was employed. Substitution of piperidine for sodium ethoxide as the condensing agent in ethanol solution was also unsuccessful.

Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcylic ester (6·4 g.) was heated in 10% aqueous sodium hydroxide for about 15 min. at 70°, until a small portion gave no precipitate when acidified. The bulk of the solution was then acidified and boiled, *dihydro-5-o-nitrostyrylresorcinol* separating as a dark brown solid, which crystallised from aqueous ethanol as a yellow microcrystalline powder, m. p. 141° (3 g., 60%) (Found: C, 65·0; H, 5·2; N, 5·2. $C_{14}H_{13}O_4N$ requires C, 64·9; H, 5·1; N, 5·4%).

[12] Diehl and Einhorn, *Ber.*, 1885, **18**, 2327.

Condensation of o-Nitrocinnamaldehyde with Ethyl Malonate.—A mixture of ethyl malonate (9 g., 1 mol.), *o*-nitrocinnamaldehyde (10 g., 1 mol.), and piperidine (0·2 c.c.) was kept in a closed flask for 2 days and then heated on a water-bath for 16 hr. Ether was then added and the solution washed with acid and water, and dried (Na_2SO_4). Removal of ether and distillation under reduced pressure yielded unchanged ethyl malonate and then a light yellow oil, of which only a small quantity could be collected, since much charring occurred owing to presence of unchanged aldehyde. The yellow oil solidified and crystallised from aqueous acetone, to give *ethyl 2-nitrocinnamylidenemalonate* as short yellow needles, m. p. 92° (1·8 g., 10%) (Found : C, 60·3; H, 5·2. $C_{14}H_{17}O_6N$ requires C, 60·2; H, 5·4%).

Action of Phosphorus Trichloride on Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcinol (3 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus trichloride (0·8 g., 1 mol.) for 3 hr. The mixture was washed several times with 4% aqueous sodium hydroxide and then water, and the chloroform layer dried ($CaCl_2$). Evaporation of the chloroform gave a yellow oil (1·75 g., 54%) which solidified and crystallised from aqueous ethanol, to yield *3-chloro-5-o-nitrostyrylcyclohex-2-en-1-one* as yellow needles, m. p. 55° (Found : C, 60·6; H, 4·3. $C_{14}H_{12}O_3NCl$ requires C, 60·5; H, 4·4%).

If the usual procedure, removal of chloroform and then washing with alkali, was employed, the chloro-ketone was hydrolysed very rapidly to the original dihydroresorcinol.

Action of Phosphorus Pentachloride on Dihydro-5-o-nitrostyrylresorcinol.—(*a*) The dihydroresorcinol (2 g., 1 mol.) was suspended in dry chloroform (10 c.c.), and phosphorus pentachloride (3·2 g., 2 mol.) added gradually. The mixture was heated for 4 hr. and, by following the usual procedure of evaporating the chloroform and extracting with ether, a yellow oil was obtained. It was passed in ether through a short column of neutralised alumina. The ether eluates yielded 3 : *5-dichloro-2′-nitrostilbene* (1·45 g., 64%), which crystallised from aqueous ethanol as yellow needles, m. p. 136° (Found : C, 57·5; H, 3·4. $C_{14}H_9O_2NCl_2$ requires C, 57·2; H, 3·1%).

(*b*) The dihydroresorcinol (2 g., 1 mol.) was suspended in chloroform (10 c.c.), phosphorus pentachloride (6·4 g., 4 mol.) added in small quantities, and the mixture heated for 4 hr. The usual procedure gave 3 : 5-dichloro-2′-nitrostilbene (1·9 g., 84%), which solidified almost immediately and crystallised from aqueous ethanol in small yellow needles, m. p. and mixed m. p. 136°.

Action of Phosphorus Tribromide on Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcinol (2 g., 2 mol.) was suspended in chloroform (10 c.c.) and heated with phosphorus tribromide (1·05 g., 1 mol.) for 3 hr. Subsequent procedure yielded a yellow oil which was passed in ether through a column of neutralised alumina (30 g.). On elution with ether *3-bromo-5-o-nitrostyrylcyclohex-2-en-1-one* was obtained. This solidified (1 g., 40%), and crystallised from aqueous methanol in pale yellow plates, m. p. 70° (Found : C, 52·3; H, 3·6. $C_{14}H_{12}O_3NBr$ requires C, 52·2; H, 3·8%).

Action of Bromine on Dihydro-5-o-nitrostyrylresorcinol.—Bromine (4 g., >3 mol.) in dry chloroform (30 c.c.) was added during 2 hr. to a suspension of the dihydroresorcinol (1·3 g., 1 mol.) in chloroform (15 c.c.), a pasty brown solid separating. Next day the solid was filtered off and dried over sodium hydroxide. Crystallisation from aqueous acetone yielded 2 : *2-dibromodihydro-5-o-nitrostyrylresorcinol* as a pale yellow microcrystalline powder, m. p. 146° (Found : Br, 39·3. $C_{14}H_{11}O_4NBr_2$ requires Br, 38·4%).

One of us (D. A. D.) acknowledges a grant from the Swansea Local Education Authority.

UNIVERSITY COLLEGE, SWANSEA, UNIVERSITY OF WALES. [*Received, July 23rd,* 1956.]

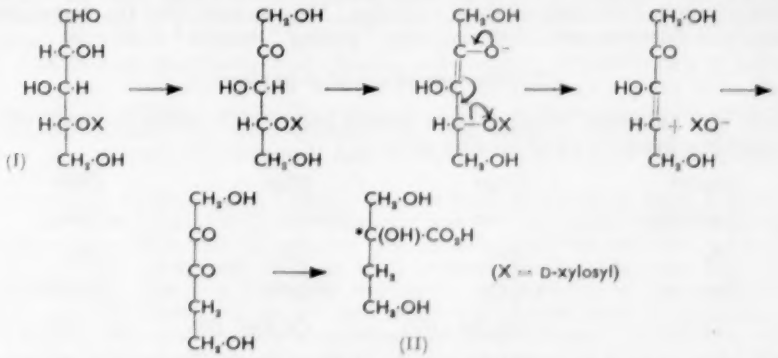
938. *The Degradation of Xylobiose and Xylotriose by Alkali.*

By G. O. Aspinall, (Miss) Mary E. Carter, and (in part) M. Los.

The 1 : 4-lactone of (±)-2 : 4-dihydroxy-2-hydroxymethylbutanoic acid (xylo*iso*saccharinolactone) has been synthesised from 1 : 4-diacetoxybutan-2-one. The alkaline degradation of xylobiose and xylotriose has been studied, and xylo*iso*saccharinolactone has been identified as a major degradation product.

The xylans, which constitute the major fraction (other than cellulose) of the cell-wall polysaccharides of many land plants, normally require the use of alkaline solutions for their removal from the plant. Structural studies [1] have shown that all the xylans so far examined from land plants contain a backbone of 1 : 4-linked β-D-xylopyranose residues, but that the several xylans differ in the number, nature, and mode of linkage of the sugar residues attached as side-chains. We have little knowledge, however, of the extent to which these polysaccharides may have undergone structural modification during their isolation by a process analogous to the alkaline degradation of reducing sugars.[2] We now report on the alkaline degradation of 4-*O*-β-D-xylopyranosyl-D-xylopyranose (xylobiose) (I) and xylotriose, oligosaccharides chosen as model compounds containing the 1 : 4-linkages typical of the xylans. Since the appearance of a preliminary account [3] of some of the following results, Whistler and Corbett [4] have published the results of a similar investigation.

It would be expected from work by Corbett, Kenner, and Richards [2] that 1 : 4-linked xylo-oligosaccharides [*e.g.* xylobiose (I)] would be degraded by alkali with the formation of xylo*iso*saccharinic acid (II). This acid contains only one asymmetric carbon atom, marked *, and if degradation proceeds by the type of mechanism indicated involving a benzilic acid rearrangement in the final stage a racemic product would be expected. To facilitate subsequent studies this acid was synthesised. 1 : 4-Diacetoxybutan-2-one, prepared by the hydration of butyne-1 : 4-diol diacetate,[5] was converted into the cyano-



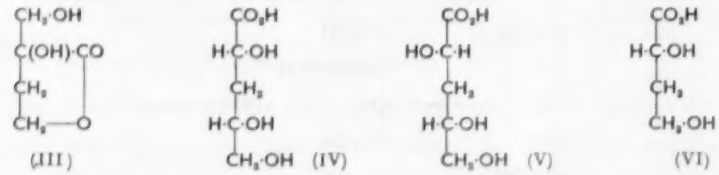
hydrin; hydrolysis of the crude cyanohydrin, which was accompanied by removal of the acetyl groups and lactonisation, yielded the 1 : 4-lactone (III) of (±)-2 : 4-dihydroxy-2-hydroxymethylbutanoic acid (II). The structure of the lactone was confirmed by the isolation of formaldehyde and α-tetronic acid [6] on periodate oxidation.

[1] Hirst, *J.*, 1955, 2974.
[2] Corbett, Kenner, and Richards, *J.*, 1955, 1810, and previous papers in the series "The Degradation of Carbohydrates by Alkali."
[3] Aspinall, Carter, and Los, *Chem. and Ind.*, 1955, 1553.
[4] Whistler and Corbett, *J. Amer. Chem. Soc.*, 1956, **78**, 1003.
[5] Lozac'h, *Bull. Soc. chim. France*, 1944, **11**, 514.
[6] Schinz and Hinder, *Helv. Chim. Acta*, 1947, **30**, 1349.

Although most recent studies of the alkaline degradation of carbohydrates [2] have involved the use of lime-water, we have investigated the action of *ca.* N-sodium hydroxide (in the absence of oxygen) on xylobiose (I) and xylotriose in order to simulate the conditions normally employed in the extraction of xylans from lignified tissues. Preliminary experiments showed that the reaction patterns were similar with both reagents and we have already reported the isolation of the lactone (III) from the reaction of lime-water on xylobiose.[3] Paper chromatography showed that xylobiose when treated with alkali produced four lactones, one of which travelled at the same rate as the synthetic lactone (III). The other three lactones were also detected as products of the alkaline degradation of D-xylose and it is probable that these were the lactones of the isomeric "*erythro*"- and "*threo*"-D-2 : 4 : 5-trihydroxypentanoic acids (IV and V) and of 2 : 4-dihydroxybutanoic acid (VI) isolated by Nef from the action of 8N-sodium hydroxide on D-xylose.[7] The *iso*lactone (III) could not be detected amongst the degradation products of D-xylose. When an acid-degraded esparto xylan was treated with N-sodium hydroxide, chromatographic examination of the products showed the presence of the *iso*lactone and an unknown substance which moved more slowly on the chromatogram; the three lactones known to be formed from xylose could not be detected. The unknown substance was an ester or lactone which yielded xylose and the *iso*lactone on hydrolysis; insufficient of this compound was available for a full characterisation, so that its importance as a product cannot be assessed. It is possible, however, that the compound was a reversion product derived from xylose and the *iso*lactone as a chromatographically similar substance was shown to be produced when an alkaline solution of the acid (II) and D-xylose was de-ionised with cation-exchange resin and concentrated; as no lactones of the acids (IV), (V), and (VI) were detected during the xylan degradation it is unlikely that xylose was formed as a reaction intermediate, but it is possible that xylose might have been produced by the hydrolysis of unchanged xylan during the concentration of the acidic products. The absence of the lactonisable acids (IV), (V), and (VI) during the xylan degradation suggests that these straight-chain acids arise only from xylose, and that their presence amongst the degradation products of xylobiose and xylotriose indicates the formation of xylose in the course of the reaction of these oligosaccharides with alkali—xylose, indeed, was detected chromatographically in these reactions. This suggests that the degradation of xylobiose and xylotriose with alkali involves a "peeling" reaction [8] of the type

xylotriose ⟶ xylobiose ⟶ xylose

in which each successive reducing sugar residue gives rise to acidic products with the simultaneous exposure of a new reducing group.



(III) (IV) (V) (VI)

Xylo*iso*saccharinolactone (III) was isolated by chromatography from the products of the action of *ca.* N-sodium hydroxide on both xylobiose and xylotriose, and was identical with the synthetic lactone. In neither case was optical activity observed. It is possible that the low optical activity observed for the similar product isolated by Whistler and Corbett [4] either arose from a contaminant or resulted from a partial resolution during its separation *via* the brucine salt.

Quantitative measurements of the acids produced during the alkaline degradations were carried out by a modification [8] of Bamford, Bamford, and Collins's method,[9] in which

[7] Nef, *Annalen*, 1910, **376**, 1.
[8] Kenner and Richards, *J.*, 1954, 1784.
[9] Bamford, Bamford, and Collins, *Proc. Roy. Soc.*, 1950, *A*, **204**, 85.

the lactonisable and non-lactonisable acids were differentiated. From the quantities of lactonisable acids formed from xylose, xylobiose, and xylotriose (0·35, 0·75, and 1·16 mol., respectively), taken together with the quantities of xylo*iso*saccharinolactone isolated from xylobiose and xylotriose (0·38 and 0·82 mol.), it is reasonable to conclude that the same quantities of acids (IV), (V), and (VI) are produced in each case, and that the additional quantities of lactonisable acid formed from xylobiose and xylotriose can be accounted for in terms of the *iso*saccharinolactone. Such an observation is again consistent with a "peeling" mechanism for the alkaline degradation of xylobiose and xylotriose. It is clear, however, from these quantitative measurements that the degradations also result in the formation of non-lactonisable acids and that formation of saccharinic acid is not the only reaction in which glycosidic bonds are broken with the exposure of new reducing groups.

Experimental

Paper-partition chromatography was carried out on Whatman No. 1 filter paper with the following solvent systems (v/v): (A) ethyl acetate–pyridine–water (10 : 4 : 3); (B) butan-1-ol–formic acid–water (500 : 115 : 385; top layer); and (C) ethyl acetate–acetic acid–water (10 : 1·3 : 1).

1 : 4-*Lactone of* (±)-2 : 4-*Dihydroxy-2-hydroxymethylbutanoic Acid* (*Xylo*isosaccharinolactone).—1 : 4-Diacetoxybutan-2-one [8] (15·9 g.) was shaken with a solution of sodium metabisulphite (16 g.) in water (40 ml.), and a solution of potassium cyanide (10 g.) in water (25 ml.) then added slowly with shaking during 0·5 hr., the temperature being maintained at 0°. The mixture was extracted with ethyl acetate and the extract was evaporated. The resulting syrup was hydrolysed with a mixture of concentrated hydrochloric acid (20 ml.) and water (30 ml.) at 60° for 2 hr. and set aside overnight at room temperature. Acid was removed by distillation, the dry residue was extracted with ethyl acetate, and the extract filtered; after partial removal of solvent the 1 : 4-*lactone* of 2 : 4-*dihydroxy-2-hydroxymethylbutanoic acid* (6·2 g.) crystallised on cooling. After recrystallisation from ethyl acetate the lactone (5·8 g.) had m. p. 95·5—96·5° (Found: C, 45·6; H, 6·2. $C_5H_8O_4$ requires C, 45·5; H, 6·1%).

*Periodate Oxidation of Xylo*isosaccharinolactone.—(a) *Identification of formaldehyde.* Sodium metaperiodate solution (5 ml.; *ca.* 0·3M) was added to a solution of the lactone, and set aside overnight. Excess of periodate was destroyed according to Bell's procedure [10] and addition of dimedone (160 mg.) in ethanol (2 ml.) yielded the formaldehyde derivative, m. p. and mixed m. p. 189—190°.

(b) *Identification of α-tetronic acid.* Sodium metaperiodate solution (1·78 g. in 175 ml. of water) was added slowly during 6 hr. to a solution of the lactone (1·11 g.) in water (25 ml.). Next morning the solution was extracted with ether for 6 hr. Evaporation yielded a solid which, after four sublimations and two recrystallisations from benzene, had m. p. 109—110° and mixed m. p. 106—109° (with α-tetronic acid, synthesised by Schinz and Hinder's method; [9] m. p. 105—106°).

Preparation of Xylobiose and Xylotriose.—Esparto hemicellulose (50 g.) was shaken in water (750 ml.) for 24 hr., water (3·25 l.) and N-sulphuric acid (1 l.) were added, and the mixture was heated on a boiling-water bath for 100 min. The cooled solution was neutralised with sodium hydrogen carbonate and set aside for 48 hr. at 4°. A small quantity of degraded esparto xylan separated and was used in a subsequent experiment. The solution was concentrated and poured on charcoal–Celite (1 : 1, 56 × 7 cm.); elution with water removed monosaccharides (xylose together with small amounts of arabinose) and inorganic salts. Elution with ethanol–water (1 : 19; 13 l.) and ethanol–water (3 : 17; 6 l.) yielded fractions 1 (4·2 g.) and 2 (2·5 g.), consisting largely of xylobiose and xylotriose respectively. Final purifications were effected by chromatography on filter sheets (Whatman 4MM), solvent A being used. A sample of xylobiose was crystallised from aqueous methanol containing a little light petroleum (b. p. 60—80°) and had m. p. and mixed m. p. 183—187°. The xylotriose was characterised by conversion into the octa-acetate, m. p. 110° (Whistler and Tu [11] report m. p. 109—110°).

Determination of Acids Produced by the Action of Alkali on Xylose, Xylobiose, and Xylotriose.—Chromatographically pure sugars were dissolved in carbonate-free sodium hydroxide solution (25 ml.) under oxygen-free nitrogen. The mixture was set aside at room temperature (16—18°).

[10] Bell, *J.*, 1948, 992.
[11] Whistler and Tu, *J. Amer. Chem. Soc.*, 1952, **74**, 4334.

and samples (2 ml.) were withdrawn periodically and were de-ionised by passing through a column (35 × 1·2 cm.) of Amberlite resin IR-120(H) (*ca.* 25 g.). The column was then washed with water (30 ml.), and the eluate was titrated potentiometrically with carbonate-free sodium hydroxide (*ca.* 0·1N). After the electrodes had been washed, the total solution was acidified with hydrochloric acid (0·5 ml.; *ca.* N) and concentrated to *ca.* 15 ml. The solution was rapidly

Sugar degraded	Time (days)	Acid (equiv./mole) total	lacton-isable	non-lacton-isable
Xylose (0·079M in 1·1N-NaOH)	3	0·74	0·26	0·48
	5	1·10	0·30	0·80
	7	1·14	0·35	0·79
Xylobiose (0·032M in 0·88N-NaOH)	1	0·55	0·31	0·24
	3	1·30	0·65	0·65
	5	1·80	0·75	1·05
	7	2·15	0·67	1·47
Xylotriose (0·0569M in 0·88N-NaOH)	1	0·78	0·59	0·19
	3	1·50	0·69	0·81
	5	2·12	0·96	1·16
	7	2·54	1·08	1·45
	9	2·84	1·10	1·74
	16	3·03	1·16	1·87

cooled and kept at room temperature for 15 min., and the non-lactonisable acids were titrated potentiometrically with carbonate-free sodium hydroxide. All operations were carried out in a nitrogen atmosphere.

Paper Chromatography of Saccharinic Acids.—Alkaline solutions were de-ionised by treatment with Amberlite resin IR-120(H) and the resulting solutions were evaporated. Saccharinic acids were detected on the chromatogram as lactones by spraying the paper with hydroxylamine followed by acidic ferric chloride as described by Abdel-Akher and Smith.[18] The lactones derived from D-xylose had R_x values of 0·62, 0·81, and 1·09 in solvent C and 0·74, 0·86, and 1·07 in solvent B (x = xylo*iso*saccharinolactone). These three lactones in addition to the *iso*-lactone were detected as degradation products from xylobiose and xylotriose.

When acid-degraded esparto xylan was treated with 1·03N-sodium hydroxide in an atmosphere of nitrogen for 28 days, paper chromatography showed the presence of two substances, giving a colour with hydroxylamine and ferric chloride and having R_x values of 0·51 and 1·0 in solvent B. A small sample of the slower-moving component was separated on filter sheets, solvent B being used; hydrolysis with 0·5N-sulphuric acid yielded the *iso*lactone and xylose, both detected chromatographically. An alkaline solution of D-xylose and the synthetic lactone was de-ionised with Amberlite resin IR-120(H) and concentrated to a syrup; chromatography showed substances having R_x values of 0·51 and 1·0.

Isolation of Xyloisosaccharinolactone from the Alkaline Degradation of Xylobiose and Xylotriose.—A solution of xylobiose (0·88 g.) in 1·1N-sodium hydroxide (carbonate-free) (35 ml.) was set aside at room temperature for 10 days in an atmosphere of nitrogen. The solution was de-ionised by passing it through Amberlite resin IR-120(H) (75 g.) and concentrated to a syrup which was fractionated on filter sheets with solvent B. Extraction of the appropriate sections of the papers yielded a chromatographically pure syrup (0·171 g.) which was crystallised from ethyl acetate to give xylo*iso*saccharinolactone, m. p. and mixed m. p. 94°, $[\alpha]_D$ 0° (*c*, 2·8 in H_2O). In a similar experiment xylotriose (0·414 g.) yielded xylo*iso*saccharinolactone (0·134 g.), m. p. and mixed m. p. 94—96°, $[\alpha]_D$ 0° (*c*, 1·8 in H_2O).

The authors thank Professor E. L. Hirst, F.R.S., for his interest and advice, Messrs. Alex. Cowan and Sons Ltd. for financial assistance (to M. E. C.), and the Rockefeller Foundation for a grant.

Department of Chemistry, University of Edinburgh. [*Received, August 7th*, 1956.]

[18] Abdel-Akher and Smith, *ibid.*, 1951, **73**, 5859.

939. *The Infrared Absorption Spectra of the Carbonyl Group in Methoxyanthraquinones, and in the Hydrochlorides of 1-Methoxyanthraquinones.*

By L. A. Wiles and L. C. Thomas.

The carbonyl stretching frequency in anthraquinones is lowered by a methoxyl group *para* to a carbonyl group. The hydrochlorides of 1-methoxyanthraquinones have not a chelate ring structure as hitherto supposed. The polyhydrochlorides show an *increase* in the carbonyl frequency, and their structure is considered.

The main purpose of this work was to investigate the structure of the hydrochlorides formed by 1-methoxyanthraquinones, but as a large number of methoxyanthraquinones were available the infrared absorption of their carbonyl groups was first examined, and the results are recorded since they extend the earlier information.

Methoxyanthraquinones.—Flett,[1] in a study of the effect of electron-donating and electron-attracting substituents on the carbonyl stretching frequency of anthraquinones, measured the infrared absorption spectra of 1- and 2-methoxy- and 1 : 4-dimethoxyanthraquinones. The carbonyl frequencies showed in each case a small change to a value 3 cm.$^{-1}$ lower than in anthraquinone. For our wider range of compounds the methoxyl group causes a marked diminution in the carbonyl frequency in some cases, while in others there is little significant difference. Dilute solutions, generally in carbon tetrachloride, were employed, but, when the solubility in this solvent was too low, chloroform was used: an examination of several methoxyanthraquinones showed that this change of solvent did not affect the position of the carbonyl band. The Nujol mull technique gave anomalous results which must be ascribed to intermolecular forces. It is significant in this connection that isomeric methoxyanthraquinones often differ considerably in melting point.

Table 1. *Methoxyanthraquinones.*

	Position of OMe	Shift of CO frequency (cm.$^{-1}$)		Position of OMe	Shift of CO frequency (cm.$^{-1}$)
1.	1-	− 3 s	10.	2 : 7-	−15 sc
2.	2-	− 3 s	11.	1 : 2 : 3-	−11 b
3.	1 : 2-	0 b	12.	1 : 2 : 4-	−11 b
4.	1 : 3-	− 8 s	13.	1 : 2 : 7-	−11 b
5.	1 : 4-	− 6 s	14.	1 : 4 : 5-	0 s
6.	1 : 5-	− 6 b	15.	1 : 2 : 5 : 8-	− 8 b
7.	1 : 8-	− 3 s	16.	1 : 4 : 5 : 8-	0 c
8.	2 : 3-	−14 b	17.	2 : 3 : 6 : 7-	−20 s
9.	2 : 6-	−15 sc			

s = sharp band; b = broad band (shift measured to mean frequency at half-band width); c = in chloroform.

Table 1 gives the results for methoxyanthraquinones. The chief points of interest are:

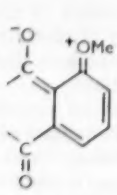
(*a*) Methoxy-substituents only in the 1-positions cause little or no change in the carbonyl frequency. This supports Flett's contention [1] that the resonance contribution of the high energy *o*-quinonoid form (I) is small. Moreover it is in these α-positions that the oppositely directed inductive effect of methoxyl will be strongest.

(*b*) (i) With a single 2-methoxy-group there is only a small frequency change. The carbonyl group at the 9-position will be unaffected by the methoxy-group, while that in the 10-position can be conjugated with a *para*-quinonoid resonance form (II). A similar contribution is evident in 1 : 3-dimethoxyanthraquinone. (ii) When *both* carbonyl groups can be influenced by *para*-quinonoid resonance the carbonyl shift is considerable (Nos. 8, 9, 11, 17). (iii) When *one* carbonyl group only can be influenced from β-positions in *different* rings the shift is again considerable (Nos. 10, 13). Shaw and Simpson [2] found recently that suitably substituted methoxy-flavanones and -flavones also show a diminution in carbonyl frequency when *para*-quinonoid resonance is possible.

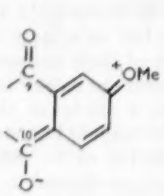
[1] Flett, *J.*, 1948, 1441.
[2] Shaw and Simpson, *J.*, 1955, 655.

The spectra of unsymmetrically substituted methoxyanthraquinones gave evidence of a splitting of the carbonyl band. Yates, Ardao, and Fieser,[3] from an infrared study of substituted *p*-benzoquinones, did not consider that the presence of two different conjugated systems necessarily led to splitting of the carbonyl band. In agreement with our results, Josien and Deschamps,[4] using a higher degree of resolution than Yates *et al.*, found that the carbonyl band is always split in unsymmetrical *p*-benzoquinones.

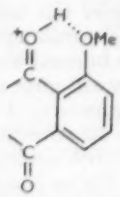
Hydrochlorides of 1-Methoxyanthraquinones.—Many polycyclic ketones (*e.g.*, xanthones, thioxanthones, and anthraquinones) which have a carbonyl in the *peri*-position to a methoxyl group are markedly basic. These halochromic compounds were extensively studied by Smiles and his co-workers, and have recently been further examined.[5,6]



(I)



(II)



(III)

Roberts and Smiles [7] suggested that the cations of these compounds have a hydrogen bond linked to methoxyl in a chelate 6-membered ring (cf. III). Before the electrostatic nature of the bond was realised it was thought that the salts owed their stability to resonance stabilization.

The methoxyl group is capable of forming chelate rings. Thus the infrared spectra of *o*-methoxyphenol [8] and *o*-methoxybenzoic acid [9] show marked shifts in the position of the hydroxyl bands.

Mesomeric structures such as (I) which have a positive ether-oxygen atom and an increased negative charge on the carbonyl-oxygen atom suggested the possibility that protonation might occur to the carbonyl oxygen (as in IV) but with no chelate ring. It was

(IV)

of interest, therefore, to study the result of hydrochloride formation on the infrared absorption of the carbonyl group in 1-methoxyanthraquinones. If formulation (III) were correct a marked diminution (or suppression) of the carbonyl frequency is to be expected, while structure (IV) would cause only a small effect.

The dihydrochlorides of the methoxyanthraquinones (methoxyl at 1 : 4-, 1 : 5-, 1 : 4 : 5-, and 1 : 4 : 5 : 8-) were prepared by passing dry hydrogen chloride over the solid anthraquinone cooled by solid carbon dioxide. Under these conditions a considerable number of mols. of hydrogen chloride were absorbed, but warming to room temperature in a stream of hydrogen chloride gave the dihydrochloride as residue. The hydrochlorides dissolved unchanged in chloroform, and the infrared spectrum of each solution so obtained was superimposed on that of the parent methoxyanthraquinone. For each hydrochloride there was a very small decrease (1—3 cm.$^{-1}$) of the carbonyl frequency.

Structure (III) is therefore incorrect. Moreover, structure (IV) in which the carbonyl group is protonated is also incorrect since there was no hydroxyl bond absorption around 3 μ. Furthermore the carbonyl frequency was only slightly perturbed, there was no marked change in the intensity of the absorption on hydrochloride formation, and the

[3] Yates, Ardao, and Fieser, *J. Amer. Chem. Soc.*, 1956, **78**, 650.
[4] Josien and Deschamps, *Compt. rend.*, 1956, **242**, 3067.
[5] Wiles, *J.*, 1952, 1358.
[6] Wiles and Baughan, *J.*, 1953, 933.
[7] Roberts and Smiles, *J.*, 1929, 1322.
[8] Wulf, Liddel, and Hendricks, *J. Amer. Chem. Soc.*, 1936, **58**, 2287.
[9] Fox and Martin, *Nature*, 1939, **143**, 199.

ultraviolet spectra of the methoxyanthraquinones and of their hydrochlorides showed no conspicuous differences.

The above-mentioned facts, and the marked instability of the hydrochlorides, is explained by weak hydrogen bonding of the carbonyl oxygen with hydrogen chloride, $>C=O \cdots H-Cl$ (V). An attempt was made to locate an H–Cl stretching frequency between 2000 and 2800 cm.$^{-1}$, but at the concentrations permissible none was found.

Recently the infrared carbonyl frequency of the polynuclear quinone, hypericin pentamethyl ether, and of its hydrochloride have been measured as dispersions in potassium bromide.[10] The parent compound absorbed at 1640 cm.$^{-1}$ and the hydrochloride at 1610 cm.$^{-1}$. The considerable difference is attributed to hydrogen bridges between the carbonyl and methoxyl groups of the type given in (III). This ether is much more basic than the methoxyanthraquinones, but it is our experience that infrared measurements of carbonyl compounds in the solid phase may be unreliable.

At low temperatures, ketones add a considerable number of molecules of hydrogen chloride in non-stoicheiometric proportions [6] and the effect on the carbonyl frequency of such addition was also examined. Dry hydrogen chloride was passed for several hours over a thin layer of the solid anthraquinone cooled by solid carbon dioxide. The highly coloured product was then rapidly transferred into chloroform and the solution stored at a low temperature until its spectrum was recorded. The results given in Table 2 were

TABLE 2.

Position of OMe	1 : 4-	1 : 5-	1 : 4 : 5-	1 : 4 : 5 : 8-
Shift (cm.$^{-1}$) of CO frequency	+34 s	0 s	+28 s	+8 b

Cf. footnotes to Table 1.

unexpected. The outstanding feature is the *increase* in carbonyl frequency, in some instances considerable. The mesomeric effect which operated in the parent compound to weaken very slightly the carbonyl link has now been suppressed, the electronic changes are reversed in direction, and the carbonyl bond is strengthened.

The literature has a few isolated examples of the strengthening of a bond on protonation. Bernstein and Martin [11] found an increase of the N–O frequency in the Raman spectra of hydroxylamine hydrochloride. Witkop [12] has shown that the infrared absorption of the $>C=N-$ group in aromatic Schiff bases and in pyridines invariably moves to shorter wavelengths on salt formation, while Hammick and Roe [13] have found that in the formation of the hydrochloride of Besthorn's Red the protonation of a nitrogen atom results in a considerable frequency increase in a neighbouring carbonyl group.

It is difficult to provide a reason for the strengthening of the carbonyl bond in the anthraquinone polyhydrochlorides. Protonation of the methoxy-group instead of the carbonyl group would have this effect, but it would then have been expected to occur in hydrochloride formation at room temperature. A possible explanation is that the additional molecules of hydrogen chloride are associated with the π-electrons of the aromatic nuclei, thereby reducing the polar nature of the carbonyl group. Brown and Brady [14] found that the solubility of hydrogen chloride in dilute solutions of aromatic compounds at $-78°$ is a measure of the basic properties of the aromatic nuclei, and they suggest that a weak interaction between the π-electrons of the ring and the polar hydrogen chloride molecule is involved.

EXPERIMENTAL

Materials.—The methoxyanthraquinones have been described,[5] but *1 : 4 : 5-trimethoxyanthraquinone* is new. Complete methylation of the 1 : 4 : 5-trihydroxy-compound was unsuccessful, and the trimethyl ether was prepared from 1 : 4 : 5-trichloroanthraquinone. 1 : 4 : 5-Trichloroanthraquinone (1 mol.) was heated with sodium methoxide (12 mols.) in methanol for 9 hr. at 165°. The product, recrystallised twice from butan-2-ol, had m. p. 209° (corr.) (Found : C, 68·3; H, 5·0; OMe, 30·5. $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7; OMe, 31·2%).

[10] Brockmann and Franck, *Naturwiss.*, 1955, **42**, 70.
[11] Bernstein and Martin, *Trans. Roy. Soc. Canada*, 1937 (III), **31**, 95.
[12] Witkop, *Experientia*, 1954, **10**, 420; *J. Amer. Chem. Soc.*, 1954, **76**, 5597.
[13] Hammick and Roe, *Chem. and Ind.*, 1953, 900.
[14] Brown and Brady, *J. Amer. Chem. Soc.*, 1952, **74**, 3570.

Absorption Spectra.—The infrared absorption spectra were obtained by means of a Perkin-Elmer Model 21, double-beam spectrophotometer fitted with a sodium chloride prism. The compounds were examined in 1% solutions in carbon tetrachloride or chloroform, in 0·2 mm. cells. The spectrum of each anthraquinone was superimposed on that of its parent compound and only the frequency shift was measured. The spectra were recorded by running the sample spectrum, reversing the instrument, and running the reference spectrum without disengaging the drum from the wavelength drive.

Thanks are offered to Mr. D. A. Swann and Mr. K. B. Tucker for assistance with the preparative work, to Imperial Chemical Industries Limited for gifts of chemicals, and to the Chief Scientist, Ministry of Supply, for permission to publish

CHEMISTRY DEPARTMENT, ROYAL MILITARY COLLEGE OF SCIENCE,
SHRIVENHAM, SWINDON, WILTS.
CHEMICAL DEFENCE EXPERIMENTAL ESTABLISHMENT,
PORTON, NR. SALISBURY, WILTS. [*Received, January 11th,* 1956.]

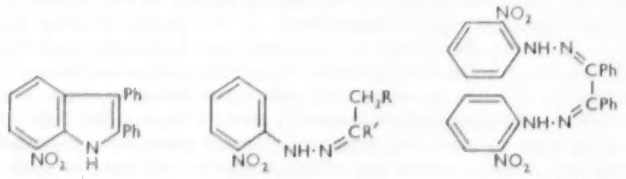
940. *The Formation of Osazones during Attempted Fischer Indole Syntheses.*

By D. A. KINSLEY and (the late) S. G. P. PLANT.

Treatment of deoxybenzoin *o*-nitrophenylhydrazone with *o*-nitrophenylhydrazine in acid solution leads to benzil di-*o*-nitrophenylhydrazone. The mechanism of this reaction is discussed. The behaviour of certain other *o*-nitrophenylhydrazones under the conditions of the Fischer indole synthesis has been investigated.

DURING attempts to prepare 7-nitro-2 : 3-diphenylindole (I) by a Fischer synthesis, deoxybenzoin *o*-nitrophenylhydrazone (II; R = R′ = Ph) was heated with acetic and hydrochloric acid. The product, however, was not the indole (I) but was identified as benzil di-*o*-nitrophenylhydrazone (III) which was synthesised from benzil and *o*-nitrophenylhydrazine.

It seemed likely that this osazone (III) was formed by reaction between the hydrazone (II; R = R′ = Ph) and free *o*-nitrophenylhydrazine obtained from it by hydrolysis since, when *o*-nitrophenylhydrazine was added to the boiling mixture of the hydrazone (II; R = R′ = Ph) and acetic and hydrochloric acids, the yield of the osazone was increased.

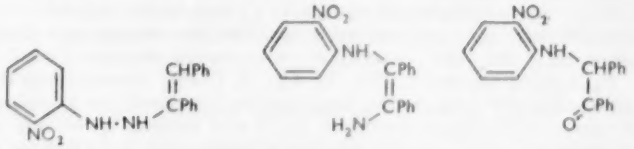


(I) (II) (III)

Further, *o*-nitroaniline was isolated from the mother-liquors of the reaction. This suggested that the oxidation of deoxybenzoin *o*-nitrophenylhydrazone to a derivative of benzil involved the corresponding reduction of *o*-nitrophenylhydrazine to *o*-nitroaniline, as occurs during the formation of the osazones of sugars.[1,2] A probable mechanism (suggested to the authors by Dr. M. J. T. Robinson) is that the tautomeric form (IV) of the hydrazone (II; R = R′ = Ph) is first converted into the vinylamine (V) by a rearrangement which is related to an *o*-semidine rearrangement [3] in the same way that the first stage

[1] Percival, "Advances in Carbohydrate Chemistry," Academic Press Inc., New York, 1948, Vol. III, p. 23.
[2] Braude and Forbes, *J.*, 1951, 1762.
[3] Cf. Hughes and Ingold, *Quart. Reviews*, 1952, **6**, 34.

of the accepted mechanism of the Fischer indole synthesis [4, 5] is related to an *o*-benzidine rearrangement. Hydrolysis of the vinylamine (V) would give the desylamine (VI) from which benzil di-*o*-nitrophenylhydrazone would be obtained by reaction with *o*-nitrophenylhydrazine,[6] either directly or by the prior formation of benzoin by further hydrolysis. In these later reactions, *o*-nitrophenylhydrazine would be reduced to *o*-nitroaniline, possibly



(IV) (V) (VI)

by the mechanism for osazone formation suggested by Braude and Forbes.[2] Robinson and Robinson [4] have previously pointed out that *o*-semidine rearrangements could occur during indole syntheses, and Dalgliesh and Mann [7] have observed the inhibiting effect of an *ortho*-substituent on certain Fischer indole reactions.

The experiments described above suggested that *o*-nitrophenylhydrazones resistant to the Fischer synthesis might give osazones under similar conditions. This was found to be the case with acenaphthenone *o*-nitrophenylhydrazone which was known not to undergo cyclisation to an indole [8] and, when acenaphthenone was heated with *o*-nitrophenylhydrazine and acetic and hydrochloric acid, acenaphthenequinone di-*o*-nitrophenylhydrazone was obtained.

Contrary to previous experience,[9] coumaranone *o*-nitrophenylhydrazone was readily converted into the corresponding indole.

It was found that, while indan-2-one *o*-nitrophenylhydrazone cyclised to 7-nitroindeno-(2′ : 3′-2 : 3)indole, the *o*-nitrophenylhydrazones of indan-1-one and propiophenone gave neither the indole nor the osazone. Further, Schofield and Theobald [10] have made 2-methyl-7-nitro-3-phenylindole from benzyl methyl ketone *o*-nitrophenylhydrazone. Now, since by the Fischer synthesis the *o*-nitrophenylhydrazones of simple aliphatic and alicyclic ketones readily provide 7-nitroindoles,[11] these results suggest that the indolisation of an *o*-nitrophenylhydrazone (II; R = alkyl or aryl) will occur if R′ is aliphatic, but will not proceed if R′ is aromatic. The example of coumaranone *o*-nitrophenylhydrazone shows, however, that this is not invariably the case.

In the reaction between 9-phenanthrol and *o*-nitrophenylhydrazine in acetic and hydrochloric acid, both indolisation and oxidation took place, leading to the formation of a mixture of 7′-nitroindolo(2′ : 3′-9 : 10)phenanthrene and phenanthraquinone *o*-nitrophenylhydrazone, *o*-nitroaniline being obtained at the same time. Since 9-phenanthrol is known to undergo aerial oxidation to phenanthraquinone,[12] it is possible that some oxidation occurred in this way during this reaction with *o*-nitrophenylhydrazine.

Experimental

Benzil Di-o-nitrophenylhydrazone.—(*a*) Deoxybenzoin *o*-nitrophenylhydrazone [13] (1·1 g.), *o*-nitrophenylhydrazine (1·5 g.), acetic acid (20 c.c.), and concentrated hydrochloric acid (10 c.c.) were refluxed together for 1½ hr., and the precipitate (0·7 g., 44%) of *benzil di-o-nitrophenylhydrazone* was collected and washed with acetic acid. It crystallised from anisole in red needles,

[4] Robinson and Robinson, *J.*, 1918, **113**, 639.
[5] Allen and Wilson, *J. Amer. Chem. Soc.*, 1943, **65**, 611.
[6] Cf. Wolf, *Chem. Ber.*, 1953, **86**, 840.
[7] Dalgliesh and Mann, *J.*, 1947, 653.
[8] Bannister and Plant, *J.*, 1948, 1247.
[9] Cawley and Plant, *J.*, 1938, 1214.
[10] Schofield and Theobald, *J.*, 1950, 1505.
[11] Perkin and Riley, *J.*, 1923, **123**, 2399; Plant, *J.*, 1929, 2493; Bauer and Strauss, *Ber.*, 1932, **65**, 308; Hughes, Lions, and Ritchie, *J. Proc. Roy. Soc. New South Wales*, 1938, **72**, 209.
[12] Japp and Findlay, *J.*, 1897, **71**, 1115.
[13] Fennell and Plant, *J.*, 1932, 2872.

m. p. 260—263°, not depressed by admixture with an authentic sample (see below) (Found: C, 65·1; H, 4·5. $C_{26}H_{20}O_4N_6$ requires C, 65·0; H, 4·2%). The acid filtrates from the Fischer reaction were diluted with water (150 c.c.), rendered alkaline with sodium hydroxide (40 g.), and, after addition of sodium sulphate (10 g.), were steam-distilled until the distillate, at first yellow, was colourless. From the latter (1200 c.c.) *o*-nitroaniline (0·4 g.), m. p. 71—73°, identified by mixed m. p., was isolated with ether.

(*b*) Benzil (0·7 g.) and *o*-nitrophenylhydrazine (1 g.) were heated together at 150° for ½ hr. The solid was washed with acetic acid and crystallised first from benzene and then from anisole, to give red needles, m. p. 261—263°, of benzil di-*o*-nitrophenylhydrazone (Found: C, 65·0; H, 4·4; N, 17·3. $C_{26}H_{20}O_4N_6$ requires C, 65·0; H, 4·2; N, 17·5%), identical with the above.

The compound, m. p. 137°, reported by Guha and De [14] as benzil di-*o*-nitrophenylhydrazone is possibly the mono-*o*-nitrophenylhydrazone, as it was formed by heating equimolecular proportions of benzil and *o*-nitrophenylhydrazine in acetic acid, but attempts to repeat the preparation led to crude material, m. p. 125—130°, which could not be purified.

Acenaphthenequinone Di-o-nitrophenylhydrazone.—(*a*) Acenaphthenone (1 g.), *o*-nitrophenylhydrazine (3 g.), acetic acid (100 c.c.), and concentrated hydrochloric acid (20 c.c.) were refluxed together for 3½ hr. The precipitate crystallised from anisole, giving crimson microcrystalline *acenaphthenequinone di-o-nitrophenylhydrazone* (0·7 g.), m. p. 297—300° (decomp.), raised to 299—301° by further crystallisation from anisole, and not depressed by admixture with an authentic sample (see below) (Found: C, 63·9; H, 3·7. $C_{24}H_{16}O_4N_6$ requires C, 63·7; H, 3·5%).

(*b*) Acenaphthenequinone [15] (0·9 g.) and *o*-nitrophenylhydrazine (1·5 g.) were heated together for 50 min. at 140°. The solid crystallised from anisole as crimson, microcrystalline needles (0·9 g.), m. p. 299—301° (decomp.), of acenaphthenequinone di-*o*-nitrophenylhydrazone.

7-Nitrocoumarono(3′ : 2′-2 : 3)indole.—Coumaranone *o*-nitrophenylhydrazone [9] (1 g.) was refluxed with acetic acid (9 c.c.) and concentrated hydrochloric acid (5 c.c.) for 40 min. The product (0·5 g.) was collected and crystallised from acetic acid, giving the *indole* as red needles, m. p. 248—251° (Found: C, 67·0; H, 3·3. $C_{14}H_8O_2N_2$ requires C, 66·7; H, 3·2%).

o-Nitrophenylhydrazones.—Indan-2-one (0·6 g.) and *o*-nitrophenylhydrazine (0·7 g.) were heated together for 15 min. at 120°. Crystallisation from benzene gave *indan-2-one o-nitrophenylhydrazone* (0·7 g.) as orange needles, m. p. 173—176°, which became brown in air (Found: C, 67·1; H, 4·8. $C_{15}H_{13}O_2N_3$ requires C, 67·4; H, 4·9%). Prepared in a similar way, *indan-1-one o-nitrophenylhydrazone* separated from benzene in red needles, m. p. 212—214° (Found: C, 67·8; H, 5·0%).

7-Nitroindeno(2′ : 3′-2 : 3)indole.—After indan-2-one *o*-nitrophenylhydrazone (0·6 g.), acetic acid (10 c.c.), and concentrated hydrochloric acid (6 c.c.) had been refluxed together for 1½ hr., the solid (0·2 g.) which crystallised was purified by passing it, in benzene, through a short column of alumina. The product, obtained by evaporation, separated first from anisole and then from benzene, giving the *indole* as red needles, m. p. 234—237° (Found: C, 71·5; H, 4·0. $C_{15}H_{10}O_2N_2$ requires C, 72·0; H, 4·0%).

7′-Nitroindolo(2′ : 3′-9 : 10)phenanthrene.—9-Phenanthrol [16] (7 g.), *o*-nitrophenylhydrazine (15 g.), acetic acid (130 c.c.), and concentrated hydrochloric acid (100 c.c.) were boiled together under reflux for 3 hr. The precipitate was separated from the acid filtrates, washed with hot water, and dried. This crude mixture (8·5 g.; m. p. 205—213°) was crystallised twice from large quantities of ethyl acetate, and then from pyridine to give phenanthraquinone *o*-nitrophenylhydrazone (1·3 g.) as red needles, m. p. 247—249°, identical (mixed m. p.) with an authentic sample (see below). The mother-liquors from these crystallisations were evaporated and a portion (1·75 g.) of the residue, dissolved in benzene (1 l.), was passed through alumina (200 g.). Elution with benzene caused separation into an upper red band and a lower orange one. The latter was removed with benzene (6 l.), *7′-nitroindolo(2′ : 3′-9 : 10)phenanthrene* (0·9 g.), m. p. 255—257°, being obtained by evaporation. It separated from pyridine in orange needles, m. p. 258—260° (Found: C, 77·1; H, 3·9; N, 8·7. $C_{20}H_{12}O_2N_2$ requires C, 76·9; H, 3·8; N, 9·0%). Elution of the remaining red band with ethanol–benzene provided impure phenanthraquinone *o*-nitrophenylhydrazone.

o-Nitroaniline (0·8 g.; m. p. 69—72°) was isolated from the acid filtrates in the manner described above.

Phenanthraquinone *o*-nitrophenylhydrazone [14] was prepared by treating phenanthraquinone

[14] Guha and De, *J. Indian Chem. Soc.*, 1926, **3**, 41.
[15] *Org. Synth.*, 1944, **24**, 1.
[16] Fieser, Jacobsen, and Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2163.

(0·4 g.) in boiling acetic acid (10 c.c.) with *o*-nitrophenylhydrazine (0·3 g.). The product (0·5 g.) separated immediately and crystallised from pyridine in red needles, m. p. 246—249° (Found: C, 69·8; H, 4·0; N, 12·3. Calc. for $C_{29}H_{13}O_3N_3$: C, 70·0; H, 3·8; N, 12·3%).

The authors thank the Department of Scientific and Industrial Research for a maintenance grant (to D. A. K.).

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, July 18th*, 1956.]

---

941. *Steroids and Walden Inversion. Part XXXIV.* Solvolysis of Cholesteryl Toluene-*p*-sulphonate with Thiophenoxide Ions.*

By C. W. SHOPPEE, H. C. RICHARDS, and G. H. R. SUMMERS.

Cholesteryl toluene-*p*-sulphonate, on treatment with sodium thiophenoxide in boiling ethanol under nitrogen, affords 3 : 5-*cyclo*cholest-6-ene (8%), 6β-phenylthio-3 : 5-*cyclo*cholestane (32%), and 3α-phenylthiocholest-5-ene (13%), but 3β-phenylthiocholest-5-ene could not be detected. The structures of the last three compounds were proved by unambiguous partial syntheses.

The reaction mechanisms responsible for the formation of the above products are discussed. The experimental observations provide further evidence of the high nucleophilic power of the thiophenoxide ion, and of the abnormally great reactivity of this ion in processes involving attack on covalently bound hydrogen.

IN Part XXIII [1] of this series it was established that replacement reactions at $C_{(3)}$ in 3β-substituted Δ^5-steroids under appropriate conditions can lead to 3α-substituted Δ^5-steroids. It was also suggested that the important factors influencing the course of the reaction are the reactivity of the nucleophil and the dielectric constant of the medium. Thus replacement reactions with weakly nucleophilic reagents,[2] *e.g.*, ethoxide, methoxide, and acetate ions, proceed by a unimolecular heterolysis (S_N1) leading to retention of configuration, a result dependent on the intervention of the π-electrons of the 5 : 6-double bond in the intermediate transition state. However, with more powerful nucleophils, *e.g.* ammonia, benzylamine, this reaction pattern is accompanied by a bimolecular substitution (S_N2) with inversion of configuration at $C_{(3)}$ in which the π-electrons of the 5 : 6-double bond do not participate. In order to obtain further information concerning the effect of nucleophilic reactivity on the reaction path, the reaction of cholesteryl toluene-*p*-sulphonate with the thiophenoxide ion has been studied.

The selection of this reagent followed from its very great reactivity demonstrated in replacement reactions at carbon atoms in both aliphatic and aromatic systems. de la Mare and Vernon [3] have shown that in the reaction of thiophenoxide ion with 3 : 3-dichloroprop-1-ene bimolecular displacement (S_N2 and S_N2^1) proceeds 240 times faster than in the corresponding reaction with ethoxide ion. Quayle and Royals,[4] by comparing the reactivities of phenoxide ion and thiophenoxide ion with *n*-butyl bromide, have provided evidence that the latter nucleophil is about 1000 times the more powerful. Furthermore, Bunnet and Davis [5] have found that the reaction of thiophenoxide ion with 1-chloro-2 : 4-dinitrobenzene was immeasurably fast at 0° and that the reactivity of the thiophenoxide ion was 580 times greater than that of methoxide ion under identical conditions; they have established the following comparative scale of nucleophilic activity: thiophenoxide ion ≫ piperidine > methoxide > phenoxide ≫ hydroxide. In comparison with its extreme nucleophilic power, the thiophenoxide ion has only a small tendency to attack a proton and is therefore unlikely to cause prototropic changes or elimination reactions.

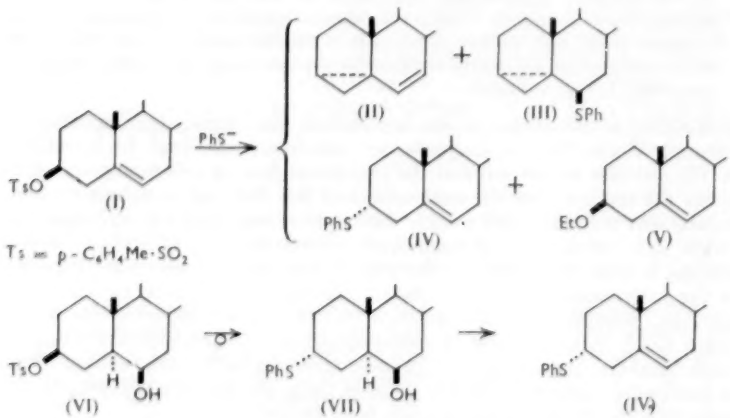
* Part XXXIII, *J.*, 1956, 2492.

[1] Shoppee, Pierce, Richards, Stephenson, and Summers, *J.*, 1955, 694.
[2] Shoppee and Westcott, *J.*, 1955, 1891.
[3] de la Mare and Vernon, *J.*, 1952, 3331.
[4] Quayle and Royals, *J. Amer. Chem. Soc.*, 1942, **64**, 226.
[5] Bunnet and Davis, *ibid.*, 1954, **76**, 3011.

Consequently it is reasonable to expect that in its reaction with 3β-substituted Δ^5-steroids, unimolecular heterolysis will be very largely superseded by bimolecular substitution, giving an increased yield of 3α-substituted Δ^5-steroid.

Previous attempts to prepare thiocholesterol derivatives by solvolysis of cholesteryl toluene-*p*-sulphonate (I) have not in general been successful. Thus this ester failed to react with boiling propane-1-thiol [6] or with ethanethiol in acetone or dioxan.[7] Treatment with thiophenol at 50° yielded a compound tentatively regarded as 3 : 5-diphenylthiocholestane, m. p. 186°, although the specific rotation, $[\alpha]_D$ −127°, appears to exclude this formulation. On the other hand, treatment of 3β-chlorocholest-5-en-7-one in acetic–hydrochloric acid with ethanethiol gave 3β-ethylthiocholest-5-en-7-one in excellent yield.[8] It is improbable that this product results directly by replacement of the chlorine atom by the mercaptan since normally inversion occurs, *e.g.*, in the acetolysis of 3β-chlorocholest-5-en-7-one ;[9] it most probably arises by 1 : 4-addition of ethanethiol to the intermediate cholesta-3 : 5-dien-7-one produced by dehydrohalogenation (cf. Ralls, Dodson, and Riegel [8]).

Extended treatment of cholesteryl toluene-*p*-sulphonate (I) with sodium thiophenoxide in boiling ethanol under nitrogen gave a complex mixture, which by repeated chromatography was separated into 3 : 5-*cyclo*cholest-6-ene,[10] m. p. 72°, $[\alpha]_D$ −43° (II) (8%),



6β-phenylthio-3 : 5-*cyclo*cholestane, $[\alpha]_D$ +34° (III) (32%), 3α-phenylthiocholest-5-ene, double m. p. 102° and 114°, $[\alpha]_D$ −43° (IV) (13%), 3β-ethoxycholest-5-ene (V) (3·5%), and diphenyl disulphide, m. p. 61° (13·5%). No detectable amount of 3β-phenylthiocholest-5-ene (IX) was formed.

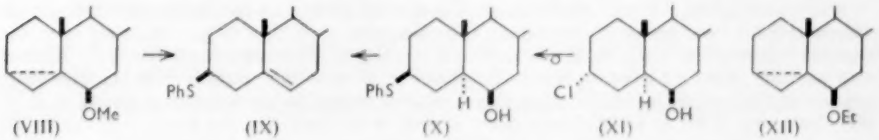
The structure of the sulphide (IV) was proved by the following partial synthesis. 6β-Hydroxycholestan-3β-yl toluene-*p*-sulphonate [11] (VI) with sodium thiophenoxide in boiling ethanol furnished, with inversion of configuration, 3α-phenylthiocholestan-6β-ol (VII), smoothly dehydrated by phosphorus oxychloride–pyridine at 15° to 3α-phenylthiocholest-5-ene (IV).

Cleavage of 6β-phenylthio-3 : 5-*cyclo*cholestane (III) with thiophenol in benzene containing sulphuric acid gave 3β-phenylthiocholest-5-ene, m. p. 72—74°, $[\alpha]_D$ −39° (IX), identical with the product obtained by rearrangement of 6β-methoxy-3 : 5-*cyclo*cholestane (VIII) in the same medium. Alternatively this sulphide (IX) was obtained by treatment of

[6] McKennis, *J. Amer. Chem. Soc.*, 1948, **70**, 675.
[7] J. C. Colbert, Ph.D. Thesis, Northwestern University, 1946, p. 51.
[8] Ralls, Dodson, and Riegel, *J. Amer. Chem. Soc.*, 1949, **71**, 3320.
[9] Shoppee, *J.*, 1946, 1149; cf. Marker, *J. Amer. Chem. Soc.*, 1937, **59**, 619.
[10] Riegel, Hager, and Zenitz, *J. Amer. Chem. Soc.*, 1946, **68**, 2562.
[11] Shoppee and Stephenson, *J.*, 1954, 2230.

3α-chlorocholestan-6β-ol [12] (XI) with sodium thiophenoxide in ethanol, followed by dehydration of the intermediate 3β-phenylthiocholestan-6β-ol (X) with phosphorus oxychloride–pyridine at 15°.

It is evident from these experiments that solvolysis of cholesteryl toluene-*p*-sulphonate in the presence of thiophenoxide ions involves a bimolecular substitution (S_N2) with



(VIII) (IX) (X) (XI) (XII)

inversion of configuration at $C_{(3)}$, to give 3α-phenylthiocholest-5-ene (IV), accompanied by a unimolecular heterolysis (S_N1) leading to 6β-phenylthio-3 : 5-*cyclo*cholestane (III) and 3 : 5-*cyclo*cholest-6-ene (II). The formation of the sulphide (IV) is consistent with the high nucleophilic power of the thiophenoxide ion.

The production of 3 : 5-*cyclo*cholestan-6β-yl sulphide (III) rather than of the 3β-Δ^5-isomeride (IX) appears to be explicable by the high nucleophilic power of the thiophenoxide ion in terms of its rate of attack on carbon; there is evidence to support the view that the equilibria involved in the 3 : 5-*cyclo*steroid rearrangement are subject to kinetic control,[13, 14, 15] so that the mesomeric cation is attacked relatively much more rapidly at $C_{(6)}$ to give (III) than at $C_{(3)}$ to yield (IX). It also seems that of the two possible elimination reactions available to the mesomeric cation, *viz.*, the formation of cholesta-3 : 5-diene and of 3 : 5-*cyclo*cholest-6-ene (II), that leading to the latter is again relatively much more rapid; the formation of (II) constitutes a case, additional to those recently reported by de la Mare and Vernon [16] and Eliel and Ro,[17] in which abnormally great reactivity of the thiophenoxide ion appears as a characteristic of rate processes involving attack on covalently bound hydrogen.

The small amount (3·5%) of 3β-ethoxycholest-5-ene (V) appears to be a primary reaction product; it does not arise by rearrangement [13] of 6β-ethoxy-3 : 5-*cyclo*cholestane (XII), since under the experimental conditions we find that 6β-ethoxy-3 : 5-*cyclo*cholestane (XII) does not rearrange to 3β-ethoxycholest-5-ene (V). We are unable satisfactorily to account for the formation of the ether (V), and we are examining the production and properties of the ethyl ethers (V) and (XII).

Experimental

$[\alpha]_D$ are measured in chloroform.

Solutions of sodium thiophenoxide were prepared by adding the theoretical quantity of thiophenol to sodium dissolved in ethanol.

3β-*Phenylthiocholest-5-ene.*—(i) 6β-Methoxy-3 : 5-*cyclo*cholestane (2 g.) in benzene (50 c.c.) containing concentrated sulphuric acid (4 drops) was refluxed with thiophenol (3 c.c.) for 18 hr. After several washings with 2N-potassium hydroxide the benzene solution on evaporation yielded an oil, $[\alpha]_D$ −23·5° (*c* 1·4) (2·1 g.), which was chromatographed on aluminium oxide (30 g.). Elution with pentane (6 × 30 c.c.) furnished an oil which by crystallisation from acetone gave 3β-*phenylthiocholest-5-ene* as plates, m. p. 72—74°, $[\alpha]_D$ −39° (*c* 1·1) (1·5 g.) [Found (after drying at 18°/0·03 mm. for 12 hr.): C, 82·4; H, 10·7. $C_{33}H_{50}S$ requires C, 82·8; H, 10·5%].

(ii) A solution of 3α-chlorocholestan-6β-ol (1 g.) and sodium thiophenoxide (3 g.) in ethanol (50 c.c.) was boiled for 18 hr. After dilution with water the product was extracted with ether, the ethereal solution washed with 2N-potassium hydroxide solution, dried, and evaporated to yield an oil (1·1 g.) which was chromatographed on aluminium oxide (30 g.). Elution with

[12] Shoppee and Summers, *J.*, 1952, 1790.
[13] Winstein and Schlesinger, *J. Amer. Chem. Soc.*, 1948, **70**, 3528.
[14] Shoppee and Nes, *J.*, in the press.
[15] Shoppee and Williams, *J.*, 1956, 2488.
[16] de la Mare and Vernon, *J.*, 1956, 41.
[17] Eliel and Ro, *Chem. and Ind.*, 1956, 251.

pentane (350 c.c.) yielded oils (400 mg.) which gave a positive Beilstein test; elution with benzene–pentane and with benzene gave oils (500 mg.) giving a positive Lassaigne test for sulphur. A solution of the last in pyridine (5 c.c.) was treated at 0° with phosphorus oxychloride (0·5 c.c.) and left for 16 hr. Working up in the usual way gave an oil (350 mg.) which was chromatographed on aluminium oxide (20 g.). Elution with pentane gave, after crystallisation from acetone, 3β-phenylthiocholest-5-ene, m. p. and mixed m. p. 72—74°.

3α-Phenylthiocholest-5-ene.—6β-Hydroxycholestan-3β-yl toluene-*p*-sulphonate (2·8 g.) in ethanol (100 c.c.) was refluxed with sodium thiophenoxide (10 g.), for 18 hr. Working up in the usual way gave an oil (3 g.) which was chromatographed on aluminium oxide (100 g.). Elution with pentane (900 c.c.) gave diphenyl disulphide, m. p. 54—56°; elution with pentane–ether gave an oil (2 g.) which by crystallisation from ethanol yielded *3α-phenylthiocholestan-6β-ol*, m. p. 107—109°, $[\alpha]_D$ +27° (*c* 1·63) [Found (after drying at 18°/0·03 mm. for 12 hr.): C, 79·3; H, 10·6. $C_{33}H_{52}OS$ requires C, 79·8; H, 10·55%]. A solution of this sulphide (1·5 g.) in pyridine (10 c.c.) was treated at 0° with phosphorus oxychloride (2 c.c.). Working up in the usual way gave a solid (1·2 g.) which by crystallisation from acetone gave *3α-phenylthiocholest-5-ene*, double m. p. 102° and 112°, $[\alpha]_D$ −42·8° (*c* 0·92) [Found (after drying at 18°/0·03 mm. for 12 hr.): C, 81·8; H, 10·1. $C_{33}H_{50}S,C_9H_6O$ requires C, 82·0; H, 10·3%].

*Reaction of Sodium Thiophenoxide with Cholest-5-en-3β-yl Toluene-*p*-sulphonate.*—(i) Cholest-5-en-3β-yl toluene-*p*-sulphonate (4·5 g.) and sodium thiophenoxide (10 g.) in ethanol (100 c.c.) were refluxed for 18 hr. Working up as described above gave a yellow oil (4·5 g.) which was chromatographed on aluminium oxide (200 g.). Elution with pentane (3 × 70; 2 × 70; 4 × 70 c.c.; and 16 × 70 c.c.) gave respectively fractions A1, m. p. 70—72° (from methanol), $[\alpha]_D$ −43° (*c* 1·2) (200 mg.); A2, an oil (300 mg.); A3, an oil (500 mg.); A4, m. p. 52—54° (from ethanol) (1·3 g.). Elution with ether–pentane (7 × 70 c.c.) gave fraction A5, a solid (1·1 g.), whilst elution with methanol and chloroform gave fraction A6, a brown oil (500 mg.). Fraction A1 consisted of pure 3 : 5-*cyclo*cholest-6-ene (mixed m. p.). Fraction A2 was rechromatographed on aluminium oxide (40 g.). Elution with pentane (1 × 50 c.c. and 5 × 50 c.c.) gave fractions B1, 3 : 5-*cyclo*cholest-6-ene, m. p. and mixed m. p. 70—72° (50 mg.), and B2, 6β-*phenylthio*-3 : 5-cyclo*cholestane*, an oil, $[\alpha]_D$ +34° (*c* 1·1) (250 mg.) [Found (after drying at 18°/0·03 mm. for 12 hr.): C, 82·9; H, 11·1. $C_{33}H_{50}S$ requires C, 82·8; H, 10·5%]. Fraction A3 was rechromatographed on aluminium oxide (50 g.). Elution with pentane (3 × 50 and 11 × 50 c.c.) gave fractions C1, 3 : 5-*cyclo*cholest-6-ene, m. p. 70—72° (50 mg.), and C2, 6β-phenylthio-3 : 5-*cyclo*cholestane, an oil, $[\alpha]_D$ +36° (*c* 0·78) (400 mg.). Fraction A4 consisted of pure diphenyl disulphide. Rechromatography of fraction A5 on aluminium oxide (40 g.) gave on elution with pentane (3 × 50 and 13 × 50 c.c.) fractions D1, an oil (50 mg.), and D2, 3α-phenylthiocholest-5-ene, m. p. 101° and 111° (1 g.). Fraction A6 was rechromatographed on deactivated aluminium oxide (20 g.). Elution with pentane (5 × 50 and 5 × 50 c.c.) gave fractions E1, an oil (150 mg.), and E2, a greasy solid (300 mg.) which after repeated recrystallisation from methanol gave cholesterol, m. p. 144—145°, $[\alpha]_D$ −41° (*c* 0·77).

(ii) Cholest-5-en-3β-yl toluene-*p*-sulphonate (9 g.) and sodium thiophenoxide (24 g.) in ethanol (500 c.c.) were refluxed under nitrogen for 65 hr. The usual working up gave an oil (7·6 g.) which was chromatographed on aluminium oxide (200 g.). Elution with pentane (1 × 70; 1 × 70; 1 × 70; 4 × 70; 11 × 70 c.c.), and ether–pentane (1 : 9) (2 × 500 c.c.) and ether–pentane (1 : 1) (6 × 500 c.c.) gave the following oily fractions: Z1 (600 mg.); Z2 (1·26 g.); Z3, $[\alpha]_D$ +40° (*c* 0·72) (980 mg.); Z4 (1·2 g.); Z5 (800 mg.); Z6 (720 mg.); and Z7 (700 mg.). Fraction Z1 was rechromatographed on aluminium oxide (15 g.), and elution with pentane (3 × 15 and 6 × 15 c.c.) gave fractions Y1, 3 : 5-*cyclo*cholest-6-ene, m. p. 69—71° (300 mg.), and Y2, 6β-phenylthio-3 : 5-*cyclo*cholestane (250 mg.). Rechromatography of Z2 on aluminium oxide (60 g.) gave on elution with pentane (4 × 15 and 10 × 15 c.c.) fractions X1, 3 : 5-*cyclo*cholest-6-ene (300 mg.), and X2, 6β-phenylthio-3 : 5-*cyclo*cholestane, $[\alpha]_D$ +35° (*c* 1·2) (65 mg.). Fraction Z3 consisted of pure 6β-phenylthio-3 : 5-*cyclo*cholestane. Fraction Z4 on rechromatography on aluminium oxide (80 g.) gave on elution with pentane (4 × 70 and 10 × 70 c.c.) fractions W1, 6β-phenylthio-3 : 5-*cyclo*cholestane, $[\alpha]_D$ +35° (*c* 0·99) (500 mg.), and W2, diphenyl disulphide, m. p. 54—56° (600 mg.). Fraction Z5 on rechromatography on aluminium oxide (30 g.) gave on elution with pentane (2 × 70 and 7 × 70 c.c.) fraction V1, diphenyl disulphide, m. p. 54—56° (400 mg.), and V2, 3α-phenylthiocholest-5-ene, double m. p. 99° and 110° (100 mg.). Fraction Z6 on rechromatography on aluminium oxide (60 g.) gave on elution with pentane (2 × 70 and 10 × 70 c.c.), fraction V1, an oil (100 mg.), and V2, 3α-phenylthiocholest-5-ene, double m. p. 100° and 111° (580 mg.). Finally, fraction Z7 on rechromatography on aluminium oxide (40 g.) gave on elution with pentane (5 × 70 and

8 × 70 c.c.) fractions T1, 3α-phenylthiocholest-5-ene, double m. p. 99° and 110° (300 mg.), and T2, 3β-ethoxycholest-5-ene, m. p. and mixed m. p. 83—84° (250 mg.).

Rearrangement of 6β-Phenylthio-3 : 5-cyclocholestane to 3β-Phenylthiocholest-5-ene.—6β-Phenylthio-3 : 5-*cyclo*cholestane (300 mg.) was refluxed for 18 hr. in dry benzene (50 c.c.) containing thiophenol (2 c.c.) and concentrated sulphuric acid (4 drops). Working up in the usual way gave a brown oil (500 mg.) which after several crystallisations from acetone gave 3β-phenylthiocholest-5-ene, m. p. 69—72°.

One of us (H. C. R.) acknowledges the award of a College Postgraduate Scholarship; we thank Glaxo Laboratories Ltd. for a gift of cholesterol.

UNIVERSITY OF WALES, UNIVERSITY COLLEGE OF SWANSEA. [*Received, July 20th,* 1956.]

---

942. *Steroids and Walden Inversion. Part XXXV. NN-Dimethylcholest-7-en-3α- and -3β-ylamine.*

By D. E. EVANS and G. H. R. SUMMERS.

Solvolysis of cholest-7-en-3α- and -3β-yl toluene-*p*-sulphonate by bases has been shown to proceed with inversion of configuration by a bimolecular mechanism. The preparation and deamination of the epimeric cholest-7-enyl-3-amines are described. The *NN*-dimethylcholest-7-en-3β-ylamine of Bertho and Baumgart [1] has been shown to be the 3α-epimeride.

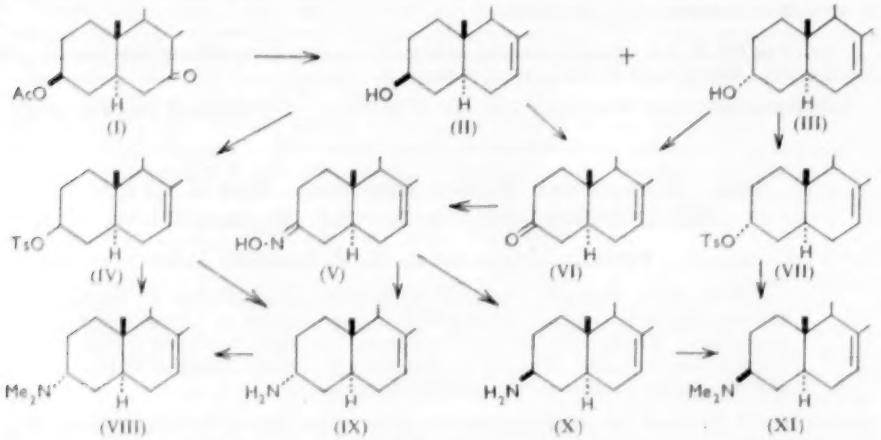
SOLVOLYSIS of the 3-toluene-*p*-sulphonates of A/B-*trans*- and A/B-*cis*-steroids by bases (*e.g.*, NH_3,[2,3] $NHMe_2$,[4,5] $C_6H_5{\cdot}CH_2{\cdot}NH_2$ [6]) proceeds by a bimolecular substitution with inversion of configuration, accompanied by some elimination. Thus cholestan-3β-yl and coprostan-3α-yl toluene-*p*-sulphonate on treatment with dimethylamine furnish *NN*-dimethylcholestan-3α-ylamine [4] and *NN*-dimethylcoprostan-3β-ylamine [5] respectively. By contrast, replacement reactions at $C_{(3)}$ in 3β-substituted Δ^5-steroids with bases (*e.g.*, NH_3, NH_2Me, $NHMe_2$, $C_6H_5{\cdot}CH_2{\cdot}NH_2$) [7] involve both a unimolecular heterolysis leading to retention of configuration at $C_{(3)}$, and a bimolecular substitution giving 3α-substituted steroid amines. Thus cholest-5-en-3β-yl toluene-*p*-sulphonate on treatment with dimethylamine yielded *NN*-dimethylcholest-5-en-3β-ylamine and *NN*-dimethyl-3 : 5-*cyclo*cholestan-6β-ylamine by the former mechanism, and *NN*-dimethylcholest-5-en-3α-ylamine by the latter mechanism.[4,5,7] In 1953 Bertho and Baumgart [1] repeated this reaction and isolated only the first product. By analogy, and possibly because of unfamiliarity with the S_N2 orientation rule,[8] Bertho and Baumgart [1] describe the product (m. p. 103—104°, $[\alpha]_D$ +17°) of the reaction of cholest-7-en-3β-yl toluene-*p*-sulphonate with dimethylamine (obtained in 72% yield) as *NN*-dimethylcholest-7-en-3β-ylamine. Although few solvolyses of 3-substituted Δ^7-steroids have been studied, it would not be expected that the π-electrons of the 7 : 8-double bond would influence replacement reactions at the distant reaction centre $C_{(3)}$ and cause retention of configuration. It was to examine the possibility of such interaction that the configuration of the supposed *NN*-dimethylcholest-7-en-3β-ylamine was investigated.

When 7-oxocholestan-3β-yl acetate (I) was subjected to the Bamford–Stevens reaction,[9] the product gave, after hydrolysis and chromatography, cholest-7-en-3α-ol (III), m. p. 176°, $[\alpha]_D$ +1° (cf. Buser [10]), and cholest-7-en-3β-ol (II), m. p. 125—127°, $[\alpha]_D$ +9° (cf.

* Part XXXIV, preceding paper.

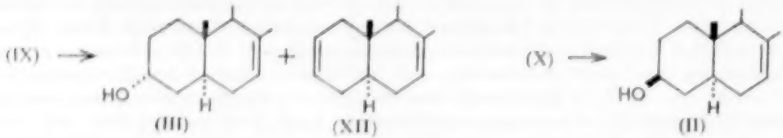
[1] Bertho and Baumgart, *Annalen*, 1953, **581**, 140.
[2] Haworth, Lunts, and McKenna, *J.*, 1955, 986.
[3] Shoppee, Evans, Richards, and Summers, *J.*, 1956, 1649.
[4] Haworth, McKenna, and Powell, *J.*, 1953, 1110.
[5] Šorm, Labler, and Czerny, *Chem. Listy*, 1953, **47**, 418.
[6] Shoppee, Richards, Sly, and Summers, *J.*, 1956, 1054.
[7] Pierce, Richards, Shoppee, Stephenson, and Summers, *J.*, 1955, 694.
[8] Ingold, "Structure and Mechanism in Organic Chemistry," George Bell and Sons, London, 1953, p. 377.
[9] Bamford and Stevens, *J.*, 1952, 4735.

Wintersteiner and Moore,[11] and Fieser [12]). Cholest-7-en-3α-ol (III) evidently results by epimerisation of the more thermodynamically stable epimeride (II), although the yield (31%) is surprisingly high for such an equilibration (cf. Windaus and Uibrig [13]). Both alcohols by oxidation with chromium trioxide in pyridine furnished cholest-7-en-3-one (IV), which was converted into its oxime (V). Reduction of the oxime with lithium



Ts = *p* - $C_6H_4Me \cdot SO_2$

aluminium hydride gave, after chromatography, cholest-7-en-3α- (IX), $[\alpha]_D$ +20°, and 3β-ylamine (X), $[\alpha]_D$ +8°, the latter being identical with the base obtained by reduction of the oxime (V) with sodium and butanol. Ammonolysis of cholest-7-en-3β-yl toluene-*p*-sulphonate (IV) also gave the amine (IX) accompanied by cholesta-2 : 7-diene (XII).



Although the configurations assigned to the bases (IX) and (X) follow from their method of preparation, confirmation was obtained by studying their reaction with nitrous acid. In a later paper [14] it will be established that, in the steroid series, equatorial amines are deaminated with retention of configuration whilst axial amines react with retention of configuration accompanied by elimination. Cholest-7-en-3β-ylamine (X) by treatment with nitrous acid gave exclusively cholest-7-en-3β-ol (II), whilst cholest-7-en-3α-ylamine (IX) afforded cholest-7-en-3α-ol (III) and cholesta-2 : 7-diene (XII). Methylation of the β-amine (X) with formaldehyde-formic acid gave *NN*-dimethylcholest-7-en-3β-ylamine (XI), also obtained by treatment of cholest-7-en-3α-yl toluene-*p*-sulphonate (IX) with dimethylamine. Methylation of the α-amine (IX) yielded *NN*-dimethylcholest-7-en-3α-ylamine (VIII), identical with the "*NN*-dimethylcholest-7-en-3β-ylamine" described by Bertho and Baumgart.[1] Consequently, the isomeric base, m. p. 78°, $[\alpha]_D$ +26°, obtained by these workers from *NN*-dimethylcholest-7-en-3α-ylamine (VIII) by treatment with platinum in acetic acid in hydrogen is *NN*-dimethylcholest-8(14)-en-3α-ylamine and not the 3β-isomer.

[10] Buser, *Helv. Chim. Acta*, 1947, **30**, 1385.
[11] Wintersteiner and Moore, *J. Amer. Chem. Soc.*, 1943, **65**, 1503.
[12] Fieser and Herz, *ibid.*, 1953, **75**, 121.
[13] Windaus and Uibrig, *Ber.*, 1914, **47**, 2384; 1915, **48**, 857.
[14] Shoppee, Evans, and Summers, *J.*, in the press.

Solvolysis of 3β-substituted Δ^7-steroids thus proceeds with inversion of configuration by a bimolecular substitution and, by contrast with the solvolysis of Δ^5-unsaturated steroids, the π-electrons of the 7 : 8-double bond do not participate in the reaction. Further evidence is provided by the acetolysis of cholest-7-en-3β-yl toluene-*p*-sulphonate (IV), which gave (after alkaline hydrolysis) cholesta-2 : 7-diene (XII) and cholest-7-en-3α-ol (III).

Experimental

$[\alpha]_D$ refer to chloroform solutions.

*3β-Acetoxycholestan-7-one Toluene-*p*-sulphonylhydrazone.*—3β-Acetoxycholestan-7-one (3·8 g.) was treated with toluene-*p*-sulphonhydrazide (2·4 g.) in refluxing ethanol for 1 hr. The solid product was crystallised from ether, to afford *3β-acetoxycholestan-7-one toluene-*p*-sulphonylhydrazone*, m. p. 235—236° (decomp.), $[\alpha]_D$ −26·4° (*c* 0·8) [Found (after drying for 3 hr. at 100°/0·03 mm.) : C, 70·2; H, 9·0. $C_{36}H_{56}O_4N_2S$ requires C, 69·7; H, 9·2%].

Cholest-7-en-3α- and -3β-ol.—3β-Acetoxycholestan-7-one toluene-*p*-sulphonylhydrazone (3·5 g.) in refluxing ethylene glycol (350 c.c.) was treated during 1 hr. with sodium (12 g.). After refluxing for a further 3 hr. the solution was cooled, treated with ethanol to destroy excess of sodium, and worked up in the usual manner, to give a solid (2·7 g.) which was chromatographed on aluminium oxide (80 g.). Elution with ether–benzene (1 : 9) gave a solid (72 mg.) which by recrystallisation from aqueous ethanol gave cholest-7-en-3α-ol as needles, m. p. 175—176°, $[\alpha]_D$ +1° (*c* 0·68). Further elution with ether–benzene (1 : 9 and 1 : 1) gave a solid (1·6 g.) which on repeated crystallisation from ethanol furnished plates of cholest-7-en-3β-ol (1·35 g.), m. p. 125—127°, $[\alpha]_D$ +9° (*c* 1·6). Crystallisation of material in the mother liquors from aqueous ethanol afforded cholest-7-en-3α-ol, m. p. 175—176° (230 mg.). Elution with ether–chloroform and chloroform gave a solid (800 mg.) which by recrystallisation from ether furnished starting material, m. p. 235—236° (decomp.).

Cholest-7-en-3-one.—Cholest-7-en-3β-ol (2 g.) in commercial pyridine (20 c.c.) was added to a solution of chromium trioxide (2 g.) in commercial pyridine (20 c.c.) prepared by the procedure of Poos, Arth, Beyler, and Sarett.[15] The solution was vigorously shaken for 0·25 hr. and kept overnight at 25°. The solution was diluted with water and worked up in the usual manner, to give a solid (1·9 g.) which was chromatographed on aluminium oxide (60 g.). Elution with pentane and benzene–pentane (1 : 4) gave a solid (1·85 g.) which by recrystallisation from acetone furnished cholest-7-en-3-one, m. p. 148°, $[\alpha]_D$ +22° (*c* 2·1).

Cholest-7-en-3-one Oxime.—Cholest-7-en-3-one (1·9 g.) was oximated in ethanol with hydroxylamine acetate. The product was crystallised from ethyl acetate, to give cholest-7-en-3-one oxime, m. p. 228° (decomp.), $[\alpha]_D$ +24·6° (*c* 0·9) [Found (after drying at 100°/0·03 mm. for 3 hr.) : C, 81·1; H, 11·05. $C_{27}H_{45}ON$ requires C, 81·1; H, 11·3%].

Cholest-7-en-3β-ylamine.—Cholest-7-en-3-one oxime (320 mg.) in refluxing butan-1-ol was treated with sodium (3 g.), and heating was continued for 3 hr. The excess of sodium was destroyed with ethanol; the product isolated in the usual manner was an oil (250 mg.) which was chromatographed on aluminium oxide (10 g.). Successive elution with ether–benzene (1 : 1), ether, and chloroform yielded cholest-7-en-3β-ylamine as an oil, b. p. 165°/0·03 mm., $[\alpha]_D$ +8° (*c* 0·9). Acetylation with acetic anhydride in ether at 15° gave a solid which by recrystallisation from acetone afforded *3β-acetamidocholest-7-ene* as plates, m. p. 252—254° (decomp.), $[\alpha]_D$ +3° (*c* 0·77) [Found (after drying at 100°/0·03 mm. for 3 hr.) : C, 81·3; H, 11·6. $C_{29}H_{49}ON$ requires C, 81·4; H, 11·5%].

Cholest-7-en-3α- and -3β-ylamine.—Cholest-7-en-3-one oxime (940 mg.) was treated with lithium aluminium hydride (800 mg.) in refluxing ether for 6 hr. The oily product (870 mg.) was chromatographed on aluminium oxide (27 g.). Elution with ether–benzene (1 : 1) and ether afforded an oil (327 mg.) which on distillation at 180—185°/0·03 mm. furnished cholest-7-en-3α-ylamine, $[\alpha]_D$ +20·3° (*c* 0·9). Acetylation with acetic anhydride in ether at 15° gave *3α-acetamidocholest-7-ene* as needles (from acetone), m. p. 202—204°, $[\alpha]_D$ +28·4° (*c* 0·68) [Found (after drying at 100°/0·03 mm. for 10 hr.) : C, 81·0; H, 11·2%]. Elution with chloroform–ether (1 : 1) and chloroform yielded an oil (351 mg.) which was distilled at 160—170°/0·03 mm., to yield cholest-7-en-3β-ylamine, $[\alpha]_D$ +8° (*c* 0·9). Acetylation with acetic anhydride in ether at 15° gave 3β-acetamidocholest-7-ene, m. p. and mixed m. p. 250—253°.

Cholest-7-en-3α-ylamine.—Cholest-7-en-3β-yl toluene-*p*-sulphonate (m. p. 104°; 700 mg.) was heated at 95° with liquid ammonia in an autoclave; the product, an oil (590 mg.), was chromatographed on aluminium oxide (18 g.). Elution with pentane–benzene (1 : 1) gave an oil

[15] Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.

(50 mg.) which by crystallisation from acetone afforded cholesta-2 : 7-diene, m. p. 72—74°. Elution with ether and chloroform gave an oil which on distillation at 180—185°/0·03 mm. furnished cholest-7-en-3α-ylamine, $[\alpha]_D$ +20° (*c* 1·1). Acetylation with acetic anhydride in ether at 15° gave 3α-acetamidocholest-7-ene, m. p. 202—204°.

Deamination of Cholest-7-en-3β-ylamine.—Cholest-7-en-3β-ylamine (200 mg.) in 50% acetic acid (20 c.c.) was treated overnight with a solution of sodium nitrite (400 mg.) in 50% acetic acid (20 c.c.). The oily product was hydrolysed with methanolic 5% potassium hydroxide solution (100 c.c.), and the product (187 mg.) chromatographed on aluminium oxide (6 g.). Elution with benzene gave a solid (130 mg.) which by recrystallisation from ethanol furnished cholest-7-en-3β-ol, m. p. and mixed m. p. 125—126°. Elution with ether gave an oil (40 mg.) which on acetylation and crystallisation from acetone yielded 3β-acetamidocholest-7-ene, m. p. 252—254° (decomp.).

Deamination of Cholest-7-en-3α-ylamine.—Cholest-7-en-3α-ylamine (120 mg.) in 50% acetic acid (20 c.c.) was treated overnight with sodium nitrite (240 mg.) in 50% acetic acid (20 c.c.). The solution was worked up in the usual manner and hydrolysed with methanolic 5% potassium hydroxide solution (20 c.c.), to furnish an oil (100 mg.) which was chromatographed on aluminium oxide (3 g.). Elution with pentane afforded an oil (35 mg.) which by crystallisation from methanol gave cholesta-2 : 7-diene, m. p. 70—72°, $[\alpha]_D$ −4° (*c* 0·9). Elution with benzene–pentane (1 : 1) gave a solid (30 mg.) which by recrystallisation from acetone furnished cholest-7-en-3α-ol, m. p. and mixed m. p. 172—174°. Elution with ether and chloroform gave an oil (25 mg.) which by acetylation furnished 3α-acetamidocholest-7-ene, m. p. 202—204°.

Cholest-7-en-3α-yl Toluene-p-*sulphonate.*—Cholest-7-en-3α-ol (300 mg.) in dry pyridine (10 c.c.) was treated with toluene-*p*-sulphonyl chloride (300 mg.) and left at 20° for 60 hr. The solid product, crystallised from methanol–acetone, gave *cholest-7-en-3α-yl toluene*-p-*sulphonate* as needles, m. p. 136°, $[\alpha]_D$ +17·3° (*c* 1·0) [Found (after drying at 100°/0·03 mm. for 10 hr.) : C, 75·6; H, 9·9. $C_{34}H_{52}O_3S$ requires C, 75·5; H, 9·7%].

NN-*Dimethylcholest-7-en-3α-ylamine.*—(*a*) Cholest-7-en-3β-yl toluene-*p*-sulphonate (500 mg.) was treated with an ethanolic solution of dimethylamine (14 c.c.; 33% w/w) in a sealed tube at 110—115° for 5 hr. The product, worked up *via* an ether-insoluble hydrochloride, gave the base (300 mg.) which by crystallisation from methanol afforded *NN*-dimethylcholest-7-en-3α-ylamine as plates, m. p. 103—104°, $[\alpha]_D$ +20° (*c* 1·0).

(*b*) Cholest-7-en-3α-ylamine (90 mg.) was treated with 90% formic acid (1·9 c.c.) and 40% formaldehyde (1·5 c.c.) at 100° for 3 hr. Isolation of the base *via* its hydrochloride afforded an oil which on crystallisation from methanol gave *NN*-dimethylcholest-7-en-3α-ylamine, m. p. and mixed m. p. 102—104°.

NN-*Dimethylcholest-7-en-3β-ylamine.*—(*a*) Cholest-7-en-3α-yl toluene-*p*-sulphonate (173 mg.) was treated with ethanolic 30% (w/w) dimethylamine (10 c.c.) in a sealed tube at 110—115° for 5 hr. The oily product (90 mg.) was chromatographed on aluminium oxide (3 g.). Elution with pentane furnished an oil (30 mg.) which by crystallisation from acetone gave cholesta-2 : 7-diene, m. p. 73—74°. Elution with benzene–pentane (1 : 1) and benzene furnished an oil (45 mg.) which by crystallisation from acetone afforded NN-*dimethylcholest-7-en-3β-ylamine*, m. p. 112—113°, $[\alpha]_D$ +12° (*c* 0·92) [Found (after drying at 80°/0·03 mm. for 3 hr.): C, 84·2; H, 12·4. $C_{29}H_{51}N$ requires C, 84·7; H, 12·4%].

(*b*) Methylation of cholest-7-en-3β-ylamine with formaldehyde and formic acid also gave *NN*-dimethylcholest-7-en-3β-ylamine, m. p. 110—112°.

Acetolysis of Cholest-7-en-3β-yl Toluene-p-*sulphonate.*—This toluene-*p*-sulphonate (645 mg.) in glacial acetic acid (15 c.c.) containing anhydrous sodium acetate (5 g.) was heated at 100° for 3 hr. The product, isolated in the usual way, was hydrolysed with lithium aluminium hydride in ether for 0·5 hr. and worked up, to give a semi-solid material (430 mg.) which was chromatographed on aluminium oxide (12 g.). Elution with pentane gave cholesta-2 : 7-diene, m. p. 70—72° (100 mg.), and elution with chloroform gave cholest-7-en-3α-ol, m. p. 170—175° (320 mg.).

One of us (D. E. E.) acknowledges the financial support of Monsanto Chemicals Ltd.; we thank Glaxo Laboratories Ltd. for performing high-pressure ammonolyses and for a gift of cholesterol. We are grateful for the interest and advice of Professor C. W. Shoppee, F.R.S.

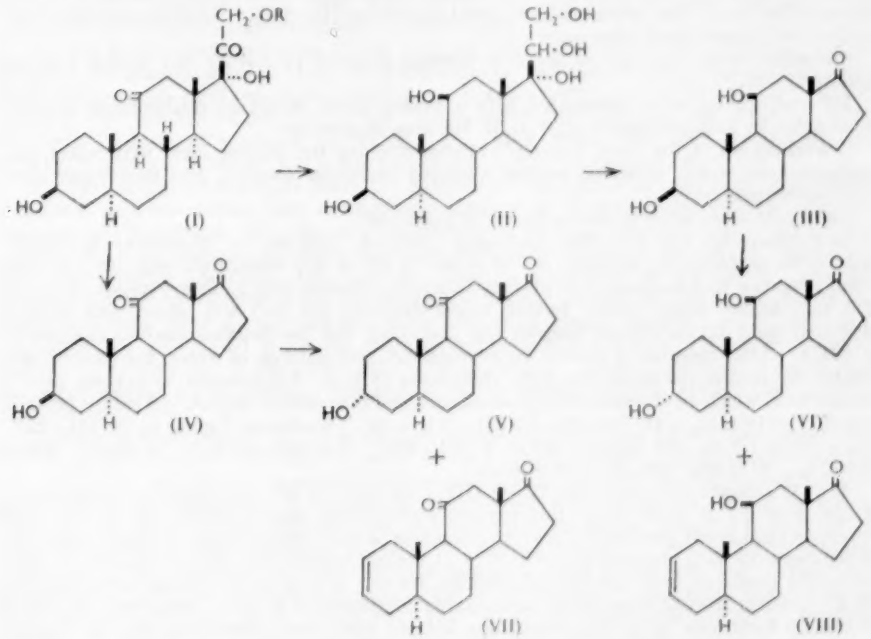
UNIVERSITY OF WALES, UNIVERSITY COLLEGE OF SWANSEA. [*Received, July 20th,* 1956.]

943. *Urinary Steroids and Related Compounds. Part I. 11-Substituted Derivatives of Androsterone.*

By W. Klyne and Sheila Ridley.

Partial syntheses of 11β-hydroxyandrosterone (3α : 11β-dihydroxy-5α-androstan-17-one) and 11-oxoandrosterone (3α-hydroxy-5α-androstane-11 : 17-dione) are described.

The compounds commonly described in biochemical literature as 11-hydroxyandrosterone (VI) and 11-keto(or oxo)androsterone (V) are minor but common constituents of human urine. The 11-hydroxy-compound was first isolated by Mason [1] and the 11-oxo-compound by Lieberman, Fukushima, and Dobriner.[2] (For further references to the presence of these compounds in urine, see ref. 3.) No partial synthesis of these two urinary steroids has hitherto been described in the literature (except for the oxidation of the 11-hydroxy- to the 11-oxo-compound); syntheses from a member of the 5α-pregnane series are now reported.



3β : 17α : 21-Trihydroxy-5α-pregnane-11 : 20-dione (I; R = H) on oxidation with sodium bismuthate in glacial acetic acid [4] gave 3β-hydroxy-5α-androstane-11 : 17-dione [5] (IV) in 68% yield. The toluene-*p*-sulphonate of this, on solvolysis with sodium acetate in acetic acid, followed by alkaline hydrolysis,[6] yielded by inversion at $C_{(3)}$ the desired 3α-isomer (V) (25%) and by elimination the related 2-ene (VII) (49%).

[1] Mason, *J. Biol. Chem.*, 1945, **158**, 719; Mason and Kepler, *ibid.*, 1945, **161**, 235.
[2] Liebermann, Fukushima, and Dobriner, *ibid.*, 1950, **182**, 299.
[3] Dorfman and Shipley, "Androgens," John Wiley and Sons, Inc., New York, 1956.
[4] Brooks and Norymberski, *Biochem. J.*, 1953, **55**, 371.
[5] Steiger and Reichstein, *Helv. Chim. Acta*, 1937, **20**, 817.
[6] Plattner and Furst, *ibid.*, 1943, **26**, 2266; Iriarte, Rosenkrantz, and Sondheimer, *J. Org. Chem.*, 1955, **20**, 542.

Solvolysis of the toluene-*p*-sulphonate of 3β : 11β-dihydroxy-5α-androstan-17-one [7] (III) [prepared from the 11 : 20-dione (I; R = Ac) by reduction with lithium aluminium hydride and oxidation with bismuthate] similarly yielded the 3α : 11β-dihydroxy-17-ketone (VI) accompanied by the 2-ene (VIII).

Samples of the partially synthetic 11-hydroxy- and 11-oxo-androsterone were kindly compared by Dr. A. E. Kellie (Courtauld Institute of Biochemistry, Middlesex Hospital Medical School, London) with samples isolated from urine, on the basis of the R_F values of the free 17-oxo-steroids and their Zimmermann complexes when run on paper chromatograms in the Bush B_1 system.[8] By these criteria, the corresponding compounds were identical. Comparisons of infrared spectra in carbon disulphide were also made. In the case of 11β-hydroxyandrosterone (run as the acetate) the records were identical. The 11-oxoandrosterone samples gave identical spectra in the carbonyl region; comparison in other regions confirmed the opinion that the material isolated from urine was impure.

Experimental

M. p.s were determined on a hot stage and are corrected.

Specific rotations were determined in chloroform (except where stated otherwise) for the sodium D line, in a 1 dm. micro-tube, at room temperature (18—25°). Analytical samples were dried at 80° (unless stated otherwise).

Chromatography was carried out with alumina supplied by Savory and Moore, Ltd., of activity II—III.[9]

Infrared spectra were determined with a Perkin-Elmer model 21 double-beam spectrophotometer, by kind permission of Dr. G. D. Meakins, Manchester.

"Working up in the usual manner" implies washing the organic layer with water, 2N-sulphuric acid, water, saturated sodium hydrogen carbonate solution, and then water until washings are neutral.

Light petroleum refers to the fraction of b. p. 60—80°.

5α-Pregnane-3β : 11β : 17α : 20β : 21-pentaol (II).—A solution of 21-acetoxy-3β : 17α-dihydroxy-5α-pregnane-11 : 20-dione (I; R = Ac) (1 g.) in dry tetrahydrofuran (25 c.c.) was added dropwise to a suspension of lithium aluminium hydride (0·5 g.) in dry tetrahydrofuran (100 c.c.) heated under reflux, further tetrahydrofuran (50 c.c.) was added, and heating continued for 2 hr. Excess of reagent was destroyed, and the reaction mixture acidified to *ca.* pH 4. After removal of solvent by evaporation, and addition of water, the product was isolated by continuous extraction with chloroform (3 hr.). Evaporation to dryness gave a gummy solid which on crystallization from alcohol, and then methyl alcohol, yielded the pentaol, m. p. 211—218°, $[\alpha]_D$ +16° (*c* 0·85 in EtOH), $[M]_D$ +59°. Reichstein [10] gives m. p. 221—222°, $[\alpha]_D$ +16° in EtOH, and Kemp *et al.*[7] m. p. 201—208°. Infrared spectrum (in Nujol): broad bands, $\nu_{max.}$ 3475 and 1020, 1049 cm.$^{-1}$ (OH).

3β : 11β-Dihydroxy-5α-androstan-17-one (III).—21-Acetoxy-3β : 17α-dihydroxy-5α-pregnane-11 : 20-dione (I; R = Ac) (5 g.) was reduced with lithium aluminium hydride (as described above) to yield crude pentaol (3·7 g.); to a solution of this, presumably a mixture of 20β- and 20α-epimers, in 50% aqueous acetic acid (1 l.) sodium bismuthate (50 g.) was added. The whole was protected from light and shaken for 1·5 hr. A solution of sodium metabisulphite (20 g.) in water (200 c.c.) was added and shaking continued for 30 min. After the addition of 3N-sodium hydroxide (1 l.) the steroid was isolated with ether–chloroform, and the organic layer washed with 3N-sodium hydroxide and water. Evaporation to dryness yielded a colourless solid (2·64 g.), which crystallized from acetone, to yield the diolone (1·65 g.), m. p. 228—233°; further material was obtained by crystallization, and chromatography from the mother-liquors. Further samples had m. p. 230—234° and 234—238°, $[\alpha]_D$ +81° (*c* 0·82), $[M]_D$ +249°, and $[\alpha]_D$ +83° (*c* 1 in EtOH), $[M]_D$ +254° {reported [7] m. p. 234—235°, $[\alpha]_D$ +84° (in EtOH)}. Infrared spectrum (in Nujol): $\nu_{max.}$ 3395, 3349 (OH), 1042 (equatorial OH), and 1720 cm.$^{-1}$ (CO). It is of interest that bands at *ca.* 1045 and 1000 cm.$^{-1}$ (3β equatorial, and 3α axial OH respectively) can be clearly distinguished in the spectra of compounds (III) and (VI), in spite of the presence in these compounds of an additional (axial) hydroxyl group at the 11β-position.

[7] Reichstein, *Helv. Chim. Acta*, 1936, **19**, 402; von Euw and Reichstein, *ibid.*, 1942, **25**, 988; Kemp, Kappas, Salamon, Herling, and Gallagher, *J. Biol. Chem.*, 1954, **210**, 123.
[8] Bush, *Biochem. J.*, 1952, **50**, 370; Kellie and Smith, *Nature*, 1956, **178**, 323.
[9] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.
[10] Reichstein, *Helv. Chim. Acta*, 1936, **19**, 29.

11β-*Hydroxy*-3β-*toluene*-p-*sulphonyloxy*-5α-*androstan*-17-*one*.—A solution of 3β : 11β-dihydroxy-5α-pregnan-17-one (1·76 g.) and freshly crystallized toluene-*p*-sulphonyl chloride (1·7 g.) in dry pyridine (8 c.c.) was kept at room temperature overnight. Excess of reagent was decomposed with iced water, and the steroid worked up *via* ether–chloroform in the usual manner; drying and evaporation of the solvent yielded a gum (2·55 g.). Trituration with ether afforded 11β-*hydroxy*-3β-*toluene*-p-*sulphonyloxy*-5α-*androstan*-17-*one* (1·41 g.) as prisms, m. p. 149—153°, and a second crop (460 mg.), m. p. 147—148°. The analytical sample had m. p. 150·5—153°, $[\alpha]_D$ +41° (*c* 1·64), $[M]_D$ +193° (Found: C, 67·95; H, 7·9. $C_{26}H_{36}O_5S$ requires C, 67·8; H, 7·9%).

11β-*Hydroxy*-5α-*androst*-2-*en*-17-*one* (VIII).—A solution of the foregoing ester (1·72 g.) and anhydrous sodium acetate (1·72 g.) in acetic acid (34 c.c.) was heated under reflux for 2 hr., then kept at room temperature for 24 hr. After removal of the acetic acid *in vacuo*, isolation *via* ether–chloroform yielded a gum, which was hydrolysed by hot 5% methanolic potassium hydroxide. The product was worked up in the usual manner in ether–chloroform, and evaporation to dryness yielded a partially crystalline gum (1·06 g.), which was chromatographed in benzene on alumina (30 g.). Elution with benzene and benzene–ether (50 : 1 and 20 : 1) yielded 11β-*hydroxy*-5α-*androst*-2-*en*-17-*one* (580 mg.) crystallizing from acetone–pentane as needles, m. p. 129—133°. Further recrystallizations gave a sample, m. p. 132·5—134°, $[\alpha]_D$ +118° (*c* 0·81), $[M]_D$ +342° (Found: C, 79·4; H, 10·0. $C_{19}H_{28}O_2$ requires C, 79·1; H, 9·8%). Infrared spectrum (in Nujol): $\nu_{max.}$ 3440 (OH), 1714 (CO), and 1653, 777 cm.$^{-1}$ (2-ene). This compound gave a yellow colour with tetranitromethane.

3α : 11β-*Dihydroxy*-5α-*androstan*-17-*one* (VI).—Further elution of the foregoing chromatogram with benzene–ether (5 : 1 to 1 : 1) yielded the 3α : 11β-diol-17-one (430 mg.), crystallizing from acetone–ether–light petroleum as prisms, m. p. 197—200°, $[\alpha]_D$ +81° (*c* 0·9), $[M]_D$ +249°, and $[\alpha]_D$ +99° (*c* 0·8 in EtOH), $[M]_D$ +309° {Mason and Kepler [9] give m. p. 199—200°, $[\alpha]_D$ +98° (in EtOH)}. Infrared spectrum (in Nujol): $\nu_{max.}$ 3492, 3344 (OH), 1000 (axial OH), and 1728 cm.$^{-1}$ (CO) (cf. Dobriner, Katzenellenbogen, and Jones,[11] compound 165).

3β : 17α : 21-*Trihydroxy*-5α-*pregnane*-11 : 20-*dione* (I; R = H).—Concentrated hydrochloric acid (10·5 c.c.) was added, with cooling, to a solution of 21-acetoxy-3β : 17α-dihydroxy-5α-pregnane-11 : 20-dione (I; R = Ac) (5 g.) in chloroform (50 c.c.), methyl alcohol (175 c.c.), and water (17 c.c.), and the mixture kept at room temperature for 48 hr. (cf. Mattox and Kendall [12]); after the addition of water (600 c.c.) the whole was kept at 4° for 24 hr., and the resulting precipitate was filtered off, washed with water and chloroform, and dried, to give the crude triol-dione (3·62 g.), crystallizing from acetone as prisms (1·95 g.), m. p. 237—244° (decomp.), $[\alpha]_D$ +70° (*c* 1·1 in EtOH), and a second crop (0·98 g.), m. p. 231—237° (decomp.) (Reichstein [7,10] gives m. p. 238—242°, $[\alpha]_D$ +66° in EtOH). Ether–chloroform extraction of the filtrate yielded a gum (0·86 g.), crystallizing to give further material (310 mg.), m. p. 222—228° (decomp.).

3β-*Hydroxy*-5α-*androstane*-11 : 17-*dione* (IV).—Sodium bismuthate (30 g.) was added to a solution of the foregoing triol-dione (1·95 g.) in 50% aqueous acetic acid (500 c.c.); and the reaction carried out in a similar manner to that described for 3β : 11β-dihydroxy-5α-androstan-17-one (above); evaporation to dryness of the ether–chloroform extract yielded the crude hydroxy-dione (1·34 g.), crystallizing from acetone–ether–pentane as prismatic needles, m. p. 168—171° (520 mg.), then needles, m. p. 164—167° (490 mg.) (lit.,[8] m. p. 166·5—168°). Chromatography of the mother-liquors (330 mg.) on alumina (10 g.) in benzene, and elution with benzene–ether (20 : 1 to 1 : 1) yielded a colourless solid (320 mg.), crystallizing from acetone–ether–pentane as needles (200 mg.), m. p. 167—168°, $[\alpha]_D$ +124° (*c* 1·47), $[M]_D$ +377°. Infrared spectrum (in Nujol): $\nu_{max.}$ 3465, 1044 (equatorial OH), and 1695, 1732 cm.$^{-1}$ (CO).

3β-*Toluene*-p-*sulphonyloxy*-5α-*androstane*-11 : 17-*dione*.—A solution of the foregoing hydroxy-dione (1·23 g.) in dry pyridine (4·5 c.c.) was treated at room temperature with freshly crystallized toluene-*p*-sulphonyl chloride (1·23 g.); working up *via* ether–chloroform in the usual manner yielded a gum (1·86 g.), crystallizing from ether to give 3β-*toluene*-p-*sulphonyloxy*-5α-*androstane*-11 : 17-*dione* as laths (1·66 g.), m. p. 160—163° (depressed on admixture with initial hydroxy-diketone), and further material (50 mg.), m. p. 152—154°. The sample for analysis had m. p. 157·5—159° before, and 153—154·5° after, drying at 40°, $[\alpha]_D$ +64° (*c* 1·42), $[M]_D$ +295° (Found: C, 67·8; H, 7·6. $C_{26}H_{34}O_5S$ requires C, 68·1; H, 7·45%).

5α-*Androst*-2-*ene*-11 : 17-*dione* (VII).—Anhydrous sodium acetate (1·71 g.) was added to the foregoing ester (1·71 g.) in acetic acid (35 c.c.), and the solution heated under reflux for 2 hr.,

[11] Dobriner, Katzenellenbogen, and Jones, "The Infrared Absorption Spectra of Steroids—An Atlas," Interscience Publ. Corp., New York.

[12] Mattox and Kendall, *J. Biol. Chem.*, 1951, **188**, 287.

then kept at room temperature overnight. Removal of the acetic acid *in vacuo*, and working up the product *via* ether–chloroform, yielded a colourless solid (1·04 g.); this was hydrolyzed with 5% methanolic potassium hydroxide (60 c.c.). Working up the product in the usual manner gave a gummy solid (960 mg.), which was chromatographed in benzene on alumina (30 g.); elution with benzene gave crude *5α-androst-2-ene*-11 : 17-*dione* (605 mg.), crystallizing from acetone as plates (496 mg.), m. p. 180—187°; a second crystallization gave material (421 mg.), m. p. 187—193°, $[\alpha]_D$ +202° (*c* 2·88), $[M]_D$ +581°. The analytical sample had m. p. 192—196° (Found: C, 79·25; H, 9·15. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·15%). Infrared spectrum (in Nujol): $\nu_{max.}$ 1699, 1734 (CO) and 1653, 773 cm.$^{-1}$ (2-ene). This compound gave a weak colour with tetranitromethane.

3α-Hydroxy-5α-androstane-11 : 17-*dione* (V).—Elution of the foregoing alumina column with benzene–ether (1 : 1; 1 : 3) gave the hydroxy-dione (357 mg.), crystallizing from acetone–ether–pentane as small laths (185 mg.), m. p. 150—151°, $[\alpha]_D$ +124° (*c* 0·95), $[M]_D$ +377°, and further material (90 mg.), m. p. 148—151°. Liebermann *et al.*[9] give m. p. 153—155°, $[\alpha]_D$ +127°. Infrared spectrum (in Nujol): $\nu_{max.}$ 3455, 999 (axial OH), 1699, 1720 cm.$^{-1}$ (CO) (cf. Dobriner, Katzenellenbogen and Jones,[11] compound 195; these authors comment that the purity of their sample was doubtful).

We are greatly indebted to Messrs. Glaxo Laboratories Ltd., Greenford, Middlesex, for a generous gift of 21-acetoxy-3β : 17α-dihydroxy-5α-pregnane-11 : 20-dione, also to Dr. G. D. Meakins under whose direction the infrared spectra were determined.

Medical Research Council, Steroid Reference Collection,
Postgraduate Medical School,
Ducane Road, London, W.12.

[*Received, August 8th*, 1956.]

---

944. *Adsorption from Binary Liquid Mixtures on Activated Alumina.*

By J. J. Kipling and D. B. Peakall.

Data for physical adsorption from binary mixtures of completely miscible liquids by different types of alumina are analysed to give the isotherms for the individual components. For a group of relatively non-polar organic liquids these can most reasonably be interpreted in terms of unimolecular adsorption. From mixtures of benzene and an aliphatic alcohol, however, the alcohol is slowly chemisorbed at 20° by the surface oxide groups to give an "alkylated" surface. Subsequent physical adsorption on this surface can be analysed and interpreted in the same way as that of the non-polar substances on the original surface of the alumina.

Theories of physical adsorption from solution have been developed largely with reference to carbon adsorbents, which have also been widely used in the practical applications of this type of adsorption. The growing importance of activated alumina, especially in chromatographic techniques, suggested that the application of current theories of adsorption to such oxide adsorbents should be considered.

Elton [1] has suggested on theoretical grounds that *selective* adsorption in this type of system is unimolecular, *i.e.*, that the adsorbed layer at the solid–liquid interface, which has a different composition from that of the bulk liquid phase, is only one molecule thick. This concept can be expressed in the equation:

$$n^s_1/(n_1)_m + n^s_2/(n_2)_m = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n^s_1 and n^s_2 are the numbers of moles of components 1 and 2, respectively, adsorbed per g. of solid, and $(n_1)_m$ and $(n_2)_m$ are the monolayer values obtained for their separate vapour isotherms. The equation is valid only if the same area of surface is available to both components.

Equation (1) has been confirmed experimentally for a carbon adsorbent by comparing

[1] Elton, *J.*, 1951, 2598

the adsorption isotherms which it gives for the individual components with those obtained from the corresponding saturated vapours.[2,3] We have now used it for analysing data obtained with alumina as the adsorbent, with a view to comparing the individual isotherms for adsorption on alumina with those for adsorption on carbon. In particular, these isotherms would be expected to throw further light on the opposite affinities shown by oxide adsorbents as compared with charcoals. Thus Bartell and his collaborators have shown that silica gel adsorbs ethyl alcohol preferentially from mixtures with benzene,[4] whereas charcoals adsorb benzene preferentially from these mixtures.[5] This follows from the shape of the isotherms of concentration change, and, for adsorption by charcoal, even more clearly from the individual adsorption isotherms.[2] In attempting to obtain the corresponding individual isotherms for adsorption on alumina, we discovered that adsorption is more complex for this system than had previously been recognised.

We may point out that the term " alumina " is used loosely to cover a range of materials of composition between Al_2O_3 and $Al_2O_3,3H_2O$. Our use of this range of materials is important not only for its possible practical implications, but also because there are phases of well-defined composition which can be recognised crystallographically. Most of the present work has been done with boehmite, the so-called monohydrate, γ-Al_2O_3,H_2O or γ-AlO·OH.* We have also used (*a*) the anhydrous oxide, γ-Al_2O_3, to provide information about the behaviour of a surface containing oxide but no hydroxide groups, (*b*) a material (referred to below as " gibbsite-type material ") with a surface similar to that of gibbsite, γ-$Al(OH)_3$, containing hydroxide but no oxide groups,† and (*c*) samples of boehmite and γ-Al_2O_3 treated with alcohols so as to modify their surfaces.

Discussion

Boehmite.—Fig. 1 shows the isotherms of concentration change for some of the systems investigated. They were analysed in terms of equation (1). For a group of relatively non-polar adsorbates, it gives individual isotherms of the general shape familiar for carbon adsorbents. The data are given in Table 1, with typical curves illustrated in Fig. 2.

Equation (1) expresses the concept of unimolecular adsorption for this type of system, but could also give a reasonable analysis into individual isotherms in some cases of multilayer adsorption. In the work on charcoal, the results were interpreted in terms of unimolecular adsorption. Indeed, the pores of the charcoal were so fine that, in most cases, the adsorbed layer could not greatly exceed a monolayer. In spite of this, Hansen and Hansen [6] proposed a " pore-filling " mechanism as an alternative interpretation of the data. From the theoretical point of view it had the drawback of giving a less specific explanation of the nature of adsorption, and, in practical terms, failed when applied in a critical case.[3]

Activated alumina has much wider pores than this charcoal, and its adsorption of single vapours involves multilayer formation and probably capillary condensation. Consequently, equilibrium adsorption from mixed saturated vapours would not readily lend itself to interpretation of liquid-phase data for such an adsorbent. The question arises, however, whether selective adsorption (as the term is used above) in adsorption from liquid mixtures is still confined, as with charcoal, to one molecular layer, or can spread to more than one layer in the wider pores of alumina.

Equation (1) is most easily interpreted in terms of filling of a specified *area* rather than a (possibly) unspecified *volume* with two types of adsorbed molecule. There are, however, three lines of experimental evidence which support the unimolecular interpretation for

* In designating the phases of alumina there is some variation between British, American, and German practice.

† Gibbsite itself has not been prepared with a high surface area, and we have therefore worked on a material which approximates to a layer of gibbsite supported on boehmite.

[2] Kipling and Tester, *J.*, 1952, 4123.
[3] Blackburn and Kipling, *J.*, 1954, 3819.
[4] Bartell, Scheffler, and Sloan, *J. Amer. Chem. Soc.*, 1931, **53**, 2501.
[5] Bartell and Sloan, *ibid.*, 1929, **51**, 1643.
[6] Hansen and Hansen, *J. Colloid Sci.*, 1954, **9**, 1.

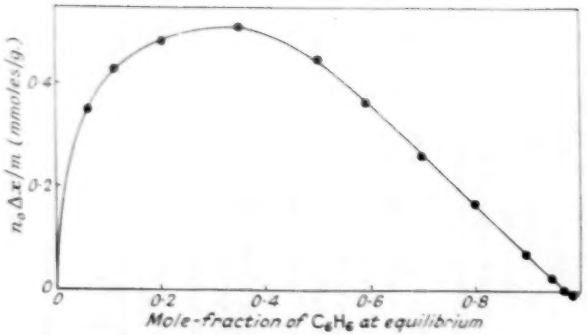


FIG. 1(*a*).

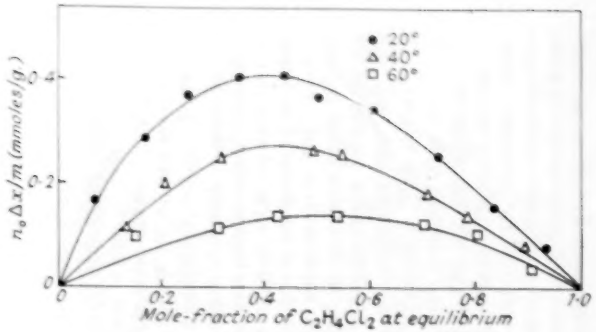


FIG. 1(*b*).

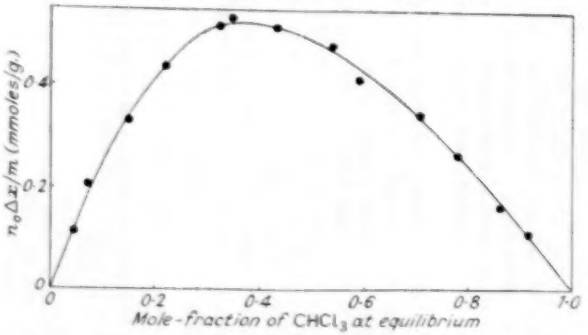


FIG. 1(*c*).

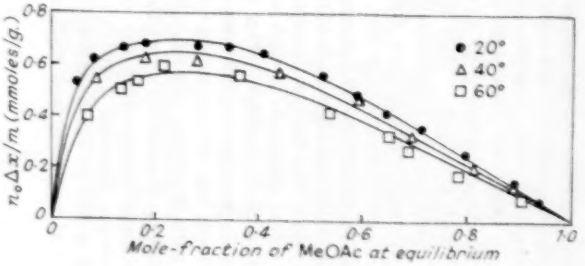


FIG. 1(*d*).

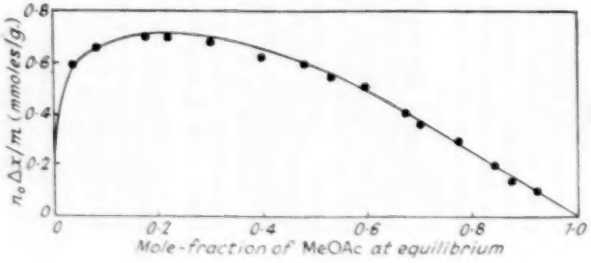


FIG. 1(*e*).

FIG. 1. *Isotherms of concentration change for adsorption on boehmite from*: (a) *benzene–cyclohexane*, (b) *ethylene dichloride–benzene*, (c) *chloroform–benzene*, (d) *methy acetate–benzene*, (e) *methyl acetate–ethylene dichloride*.

this first group of adsorbates. In the simplest theory of multilayer adsorption of *single* vapours,[7] it is assumed that the second and subsequent molecular layers are held by forces substantially equivalent to those operating in the bulk liquid (homogeneous or adsorbate–adsorbate forces), and significantly different from those holding the first layer (heterogeneous or adsorbent–adsorbate forces). This concept is now thought to be somewhat over-simplified, though as a first approximation it has been confirmed experimentally.

TABLE 1. *Individual isotherms for adsorption on boehmite from various systems.**

(a) cyclo*Hexane–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (C_6H_6)	C_6H_{12}	C_6H_6	x (C_6H_6)	C_6H_{12}	C_6H_6	x (C_6H_6)	C_6H_{12}	C_6H_6
0·0	0·99	0·00	0·4	0·26	1·01	0·8	0·10	1·24
0·1	0·62	0·52	0·5	0·20	1·10	0·9	0·07	1·30
0·2	0·47	0·72	0·6	0·16	1·15	1·0	0·00	1·37
0·3	0·35	0·88	0·7	0·13	1·20			

(b) *Ethylene dichloride–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6	x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6	x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6
0·0	0·00	1·37	0·4	0·98	0·46	0·8	1·37	0·11
0·1	0·35	1·04	0·5	1·12	0·34	0·9	1·43	0·05
0·2	0·61	0·70	0·6	1·22	0·25	1·0	1·48	0·00
0·3	0·83	0·60	0·7	1·31	0·16			

(c) *Chloroform–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x ($CHCl_3$)	$CHCl_3$	C_6H_6	x ($CHCl_3$)	$CHCl_3$	C_6H_6	x ($CHCl_3$)	$CHCl_3$	C_6H_6
0·0	0·00	1·37	0·4	1·11	0·37	0·8	1·46	0·07
0·1	0·38	1·03	0·5	1·23	0·27	0·9	1·50	0·03
0·2	0·70	0·74	0·6	1·33	0·18	1·0	1·53	0·00
0·3	0·94	0·53	0·7	1·40	0·12			

(d) *Methyl acetate–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (MeOAc)	MeOAc	C_6H_6	x (MeOAc)	MeOAc	C_6H_6	x (MeOAc)	MeOAc	C_6H_6
0·0	0·00	1·37	0·4	1·24	0·26	0·8	1·47	0·05
0·1	0·77	0·68	0·5	1·32	0·18	0·9	1·50	0·03
0·2	0·98	0·49	0·6	1·38	0·13	1·0	1·53	0·00
0·3	1·13	0·36	0·7	1·43	0·09			

(e) *Methyl acetate–ethylene dichloride*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (MeOAc)	MeOAc	$C_2H_4Cl_2$	x (MeOAc)	MeOAc	$C_2H_4Cl_2$	x (MeOAc)	MeOAc	$C_2H_4Cl_2$
0·0	0·00	1·48	0·4	1·24	0·28	0·8	1·48	0·04
0·1	0·82	0·69	0·5	1·32	0·20	0·9	1·51	0·02
0·2	1·00	0·50	0·6	1·39	0·14	1·0	1·53	0·00
0·3	1·14	0·38	0·7	1·44	0·08			

* In Tables 1—4, x is the mole-fraction of the constituent of the given formula in the liquid.

Thus the magnetic susceptibility of simple organic substances in the second and subsequent layers adsorbed on silica gel has been shown to be the same as that of the bulk liquid, though different from that of the first layer.[8]

If the same concept is applied to the adsorption of *mixtures* it would be expected that the first layer, held by heterogeneous forces, would have a different composition from that of the bulk liquid, whereas the second and subsequent layers, held by homogeneous forces, would have substantially the same composition as the bulk liquid. The second line of evidence confirms this. Cines and Ruehlen,[9] in a study of the adsorption of mixed vapours

[7] Brunauer, Emmett, and Teller, *J. Amer. Chem. Soc.*, 1938, **60**, 309.
[8] Milligan and Whitehurst, *J. Phys. Chem.*, 1952, **56**, 1073.
[9] Cines and Ruehlen, *ibid.*, 1953, **57**, 710.

on silica gel, have shown that selective adsorption is vested almost entirely in the first molecular layer.

Thirdly, Bartell and Benner [10] have calculated that the adsorbed layer at the interface between silica gel and mixtures of *iso*pentyl alcohol and *iso*octane "need not be more than of unimolecular thickness." [10] This study was accompanied by a study of the liquid–vapour interface, for which the same conclusion has long been held. By contrast, the only decisive evidence for multilayer formation at the liquid–solid interface is for adsorption from incompletely miscible substances, *e.g.*, adsorption on graphite from aqueous solutions of hexanoic and valeric acid.[11]

For the first group of adsorbates, it seems reasonable to conclude that selective adsorption is, at least to a first approximation, confined to one molecular layer.

The isotherms of concentration change for a second group of adsorbates are shown in

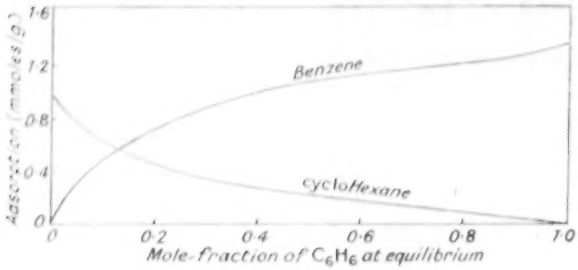


Fig. 2(*a*).

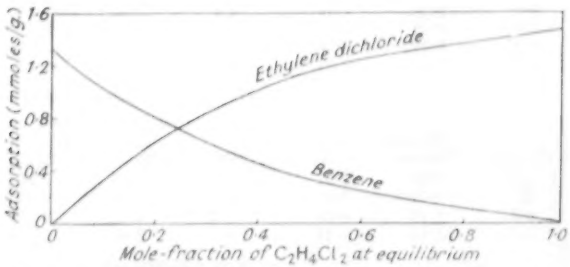


Fig. 2(*b*).

Fig. 2. *Adsorption (individual isotherms) on boehmite from*: (*a*) *benzene–cyclohexane*, (*b*) *ethylene dichloride–benzene*.

Fig. 3; each of these systems has an aliphatic alcohol as one component. These isotherms were obtained, as were those shown in Fig. 1, by shaking the adsorbent with the liquid mixtures for about 24 hours. Initially we assumed that monolayer values could be calculated from the vapour-phase isotherm for each component. It was found, however, that the maxima in the isotherms of concentration change corresponded, at the relevant concentrations, to adsorption of the respective alcohols greater than these "monolayer" values.

This is just the situation which would arise if the alcohol were adsorbed to a much greater extent than the benzene in each of several layers. It was therefore necessary to consider whether the results should be analysed in terms of the equations appropriate to multilayer formation or pore-filling.

Further experiments with boehmite, however, suggest a different explanation. In all previous experiments with this type of liquid system, adsorption equilibrium has been established well within 24 hours. For the systems containing an alcohol, however, a slow

[10] Bartell and Benner, *J. Phys. Chem.*, 1942, **46**, 847.
[11] Hansen, Fu, and Bartell, *ibid.*, 1949, **53**, 769.

change continued over a much longer period (Fig. 4), and equilibrium could not be regarded as established until about 3 weeks had elapsed. This required a re-examination of the vapour-phase experiments, and it was found that the alcohols were slowly chemisorbed by boehmite at room temperature, and that the chemisorption appeared to take place at the oxide, but not at the hydroxide groups.[12] It therefore seems likely that chemisorption of alcohols similarly takes place in the liquid phase and that by the time equilibrium has been reached, the chemisorption has extended over the whole of the available surface to give an " alkylated " alumina surface. On this new surface physical adsorption of both benzene and alcohol can follow in the normal way and would be expected to extend for only one molecular layer beyond the chemisorbed material.

The dip in the curve of $n_0\Delta x/m$ against time before the final slow rise (Fig. 4)

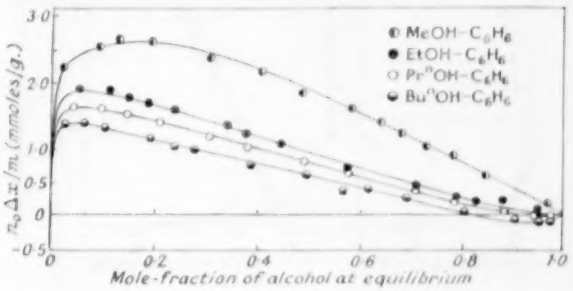


FIG. 3. *Isotherms of concentration change (after 1 day) for adsorption on boehmite from alcohol–benzene systems.*

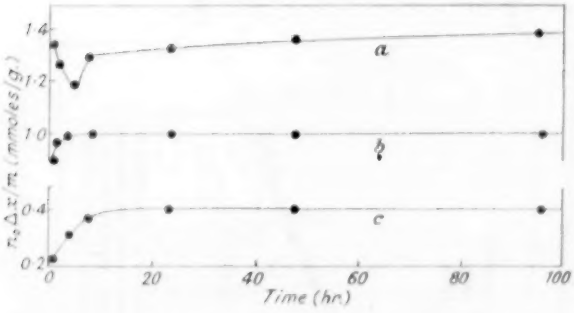


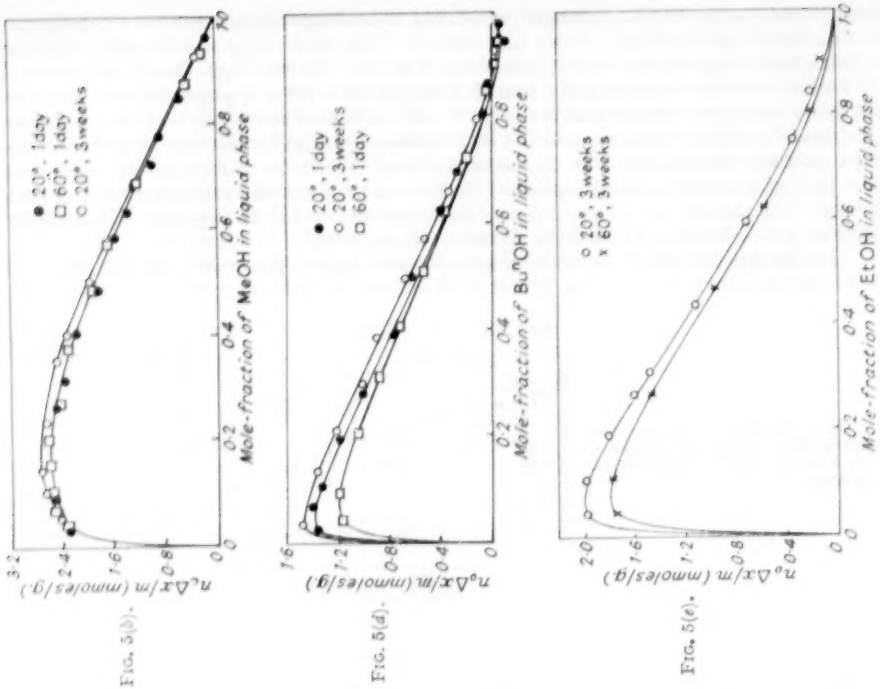
FIG. 4. *Variation of concentration change with time: (a) ethyl alcohol–benzene on boehmite, at 0·318 mole-fraction of ethyl alcohol, (b) ethyl alcohol–benzene on gibbsite-type surface, at 0·322 mole-fraction of ethyl alcohol, (c) ethylene dichloride–benzene on boehmite, at 0·331 mole-fraction of ethylene dichloride.*

is anomalous. It may result from displacement of some alcohol, initially physically adsorbed, as chemisorption proceeds; the ethyl alcohol molecule occupies a greater area when chemisorbed than when physically adsorbed.[13]

Three further observations, relating to periods shorter than are required for equilibrium with the liquid mixture to be established, support the assumption that the alcohol is in part chemisorbed. The concentration change is reduced by cooling the adsorbent during the addition of the liquid mixture, and thereby counteracting the rise in temperature due to liberation of the initial heat of adsorption. Such a rise in temperature would increase the rate of chemisorption as compared with that obtaining at the temperature of the thermostat bath (20°).

This effect of temperature has been confirmed by examining adsorption after 1 day at 20°, 40°, and 60°. For a system in which physical adsorption only takes place, there is, at the higher temperatures, an overall decrease in the preferential adsorption of the more

[12] Kipling and Peakall, *Research*, 1955, **8**, S 31.
[13] *Idem*, *J.*, in the press.



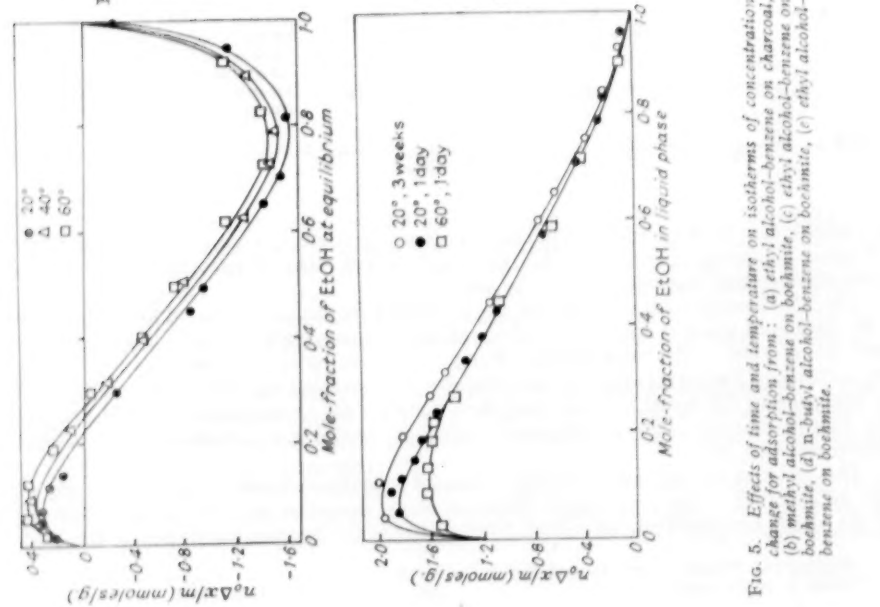


FIG. 5. *Effects of time and temperature on isotherms of concentration change for adsorption from:* (a) *ethyl alcohol–benzene on charcoal,* (b) *methyl alcohol–benzene on boehmite,* (c) *ethyl alcohol–benzene on boehmite,* (d) n-*butyl alcohol–benzene on boehmite,* (e) *ethyl alcohol–benzene on boehmite.*

strongly adsorbed component. Fig. 1(*b*) shows this for the system ethylene dichloride–benzene with boehmite; Fig. 5(*a*) shows the same effect for benzene–ethyl alcohol with charcoal. For the benzene–alcohol systems with boehmite, however, this effect is found over only part of the concentration range after 1 day's contact [Fig. 5(*b*)—(*d*)]. For the remainder, it seems that the decrease in the preferential physical adsorption has been offset by increased chemisorption. On the other hand, at equilibrium (3 weeks), the chemisorption should be the same at 20° and 60°, any difference in the isotherms at the two temperatures being due to change in physical adsorption alone and therefore extending over the whole of the concentration range. This is found in practice [Fig. 5(*e*)].

Similarly, if the system ethylene dichloride–benzene–boehmite is held for successive periods of a day at 20°, 60°, and 20°, the final position of equilibrium at 20° is the same as the original position at this temperature. With the system alcohol–benzene–boehmite, however, the effect of temperature is not reversible in this way as it should be for purely physical adsorption.

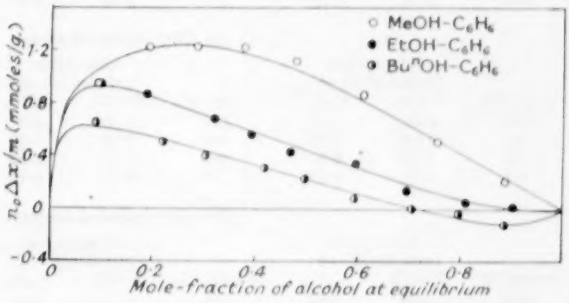


FIG. 6. *Isotherms of concentration change for physical adsorption on "alkylated" boehmites.*

Points = experimental results on "alkylated" samples; curves = calculated from results on untreated boehmite.

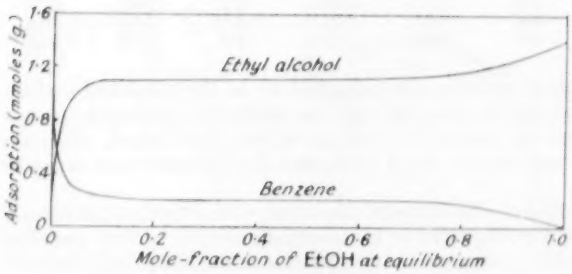


FIG. 7. *Physical adsorption (individual isotherms) on "alkylated" boehmite from ethyl alcohol–benzene.*

Any analysis of the isotherms of concentration change can only be attempted after both physical and chemical adsorption have been completed. The isotherms for this purpose were therefore determined after 3 weeks' contact between the adsorbent and the liquid mixtures (Fig. 5). The extent of chemisorption of the alcohols is known from the vapour-phase studies.[12] The effect of chemisorption on the liquid-phase adsorption can therefore be calculated and subtracted from the isotherms of concentration change to give the concentration changes due to physical adsorption only (Fig. 6).

The same separation into two stages has also been achieved experimentally. Boehmite was allowed to stand under pure ethyl alcohol for 3—4 weeks, so that the surface should become completely "ethylated" by chemisorption. The "ethylated" material, freed from excess of alcohol by evacuation, was then shaken with benzene–ethyl alcohol mixtures. Equilibrium was established in the time appropriate for physical adsorption, and the isotherm of concentration change for this stage was in agreement with that calculated by the above procedure (Fig. 6). Similar results were obtained with the other alcohols.

The curves in Fig. 6 can be analysed to show the physical adsorption of each component by using equation (1). For this purpose, it would be incorrect to use the "monolayer

values" derived from adsorption results on the untreated boehmite, as this adsorption was in part chemisorption. Instead, the adsorption of benzene vapour and of the appropriate alcohol vapour on each of the "alkylated" samples was measured and used to give monolayer values for physical adsorption. From these values, the individual isotherms for the liquid-phase adsorption were calculated (Table 2 and Fig. 7). These are of the normal

TABLE 2. *Individual isotherms for physical adsorption on boehmite from various systems.*

(a) *Methyl alcohol–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6
0·0	0·00	1·08	0·4	1·99	0·07	0·8	2·13	0·005
0·1	1·14	0·50	0·5	2·05	0·05	0·9	2·13	0·004
0·2	1·59	0·28	0·6	2·09	0·03	1·0	2·14	0·00
0·3	1·78	0·18	0·7	2·12	0·01			

(b) *Ethyl alcohol–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6
0·0	0·00	0·97	0·4	1·10	0·21	0·8	1·16	0·17
0·1	1·09	0·22	0·5	1·11	0·20	0·9	1·26	0·10
0·2	1·10	0·21	0·6	1·12	0·20	1·0	1·40	0·00
0·3	1·10	0·21	0·7	1·12	0·19			

(c) n-*Butyl alcohol–benzene*

	Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :			Adsorption (mmoles/g.) of :	
x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6
0·0	0·00	0·82	0·4	0·73	0·27	0·8	0·78	0·23
0·1	0·70	0·29	0·5	0·74	0·26	0·9	0·82	0·20
0·2	0·72	0·28	0·6	0·75	0·25	0·95	0·95	0·10
0·3	0·73	0·27	0·7	0·78	0·23	1·0	1·08	0·00

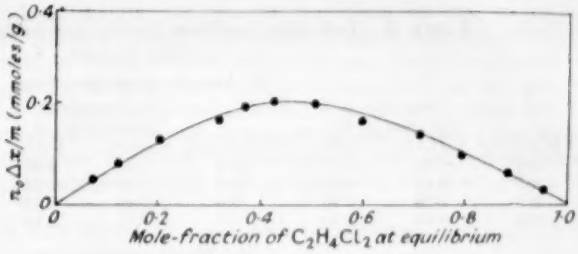
type, and show that the alcohol is preferentially adsorbed on to the alkylated surface. This might well be expected, as the surface still contains accessible hydroxide groups, which inevitably show preference for adsorption of ethyl alcohol (see below), while the chemisorbed alkyl groups may well show a slight preference for aliphatic over aromatic compounds.

γ-Alumina. As chemisorption of alcohol vapours also occurs with anhydrous alumina,[12] the liquid-phase adsorption would be expected to be essentially similar to that described for boehmite. This is borne out by experiment. Adsorption from the less polar substances follows the normal pattern for physical adsorption (Fig. 8*a*). On the other hand, adsorption from systems containing an alcohol involves chemisorption. The same effects of time and temperature are observed [Fig. 8(*b*)—(*d*)], and again only physical adsorption appears to occur on alkylated surfaces. Individual isotherms of physical adsorption for these systems are of the normal type (Table 3).

Gibbsite-type material. Chemisorption of alcohols from the vapour phase does not occur on an alumina with a purely hydroxylic ("gibbsite") surface. Adsorption from liquid mixtures containing an alcohol was therefore studied and was found to show the characteristics of physical adsorption only. Equilibrium was rapidly established (Fig. 4), the effect of temperature was that expected for physical adsorption (Fig. 9), and the isotherms of concentration change could be analysed directly in terms of unimolecular selectivity. The individual isotherms thus obtained show that the surface has a strong preference for alcohol as compared with benzene (Table 4).

General.—Our results on physical adsorption have not proved that adsorption from the systems we have studied is unimolecular. In view of the existing evidence for this type of system, the successful analysis of our data in terms of equation (1) makes it highly likely that this is so. It is particularly significant that, even in the cases of simple physical

FIG. 8(a).



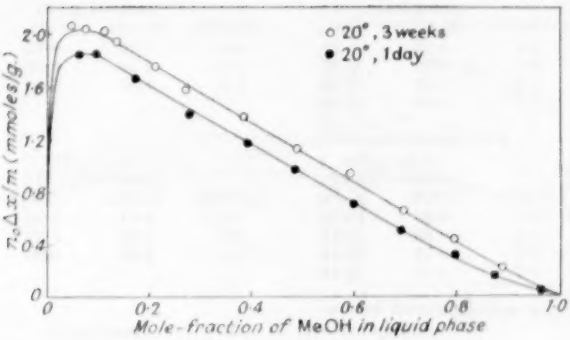
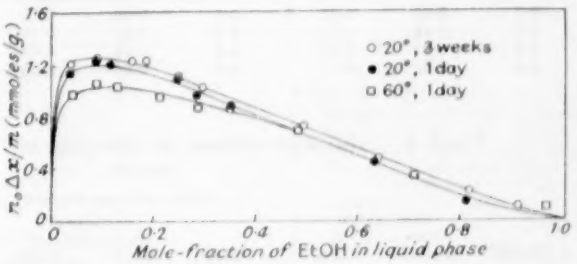


FIG. 8(b).

FIG. 8(c).



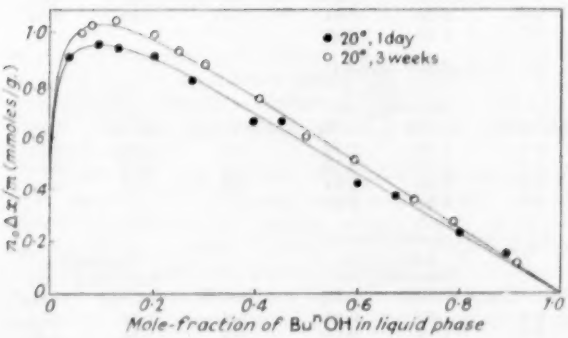


FIG. 8(d).

FIG. 8. *Isotherms of concentration change for adsorption on* γ-Al_2O_3 *from:* (a) *ethylene dichloride–benzene,* (b) *methyl alcohol–benzene,* (c) *ethyl alcohol–benzene,* (d) n-*butyl alcohol–benzene.*

TABLE 3. *Individual isotherms for physical adsorption on γ-alumina from various systems.*

(a) *Ethylene dichloride–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6	x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6	x ($C_2H_4Cl_2$)	$C_2H_4Cl_2$	C_6H_6
0·0	0·00	0·77	0·4	0·51	0·28	0·8	0·75	0·06
0·1	0·15	0·63	0·5	0·59	0·21	0·9	0·78	0·03
0·2	0·28	0·50	0·6	0·66	0·15	1·0	0·81	0·00
0·3	0·40	0·39	0·7	0·71	0·10			

(b) *Methyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6
0·0	0·00	0·71	0·4	0·89	0·29	0·8	1·19	0·15
0·1	0·80	0·33	0·5	0·92	0·27	0·9	1·30	0·09
0·2	0·82	0·32	0·6	1·00	0·22	1·0	1·49	0·00
0·3	0·86	0·30	0·7	1·09	0·19			

(c) *Ethyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6
0·0	0·00	0·57	0·4	0·68	0·16	0·8	0·74	0·12
0·1	0·63	0·19	0·5	0·69	0·15	0·9	0·83	0·07
0·2	0·63	0·19	0·6	0·71	0·14	1·0	0·95	0·00
0·3	0·67	0·16	0·7	0·72	0·14			

(d) n-*Butyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6
0·0	0·00	0·52	0·4	0·60	0·11	0·8	0·69	0·05
0·1	0·44	0·22	0·5	0·62	0·10	0·9	0·72	0·03
0·2	0·53	0·16	0·6	0·63	0·09	1·0	0·75	0·00
0·3	0·57	0·13	0·7	0·68	0·06			

TABLE 4. *Individual isotherms for adsorption on "gibbsite" from various systems.*

(a) *Methyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6	x (MeOH)	MeOH	C_6H_6
0·0	0·00	1·17	0·4	2·15	0·07	0·8	2·23	0·02
0·1	1·96	0·16	0·5	2·17	0·05	0·9	2·26	0·01
0·2	2·06	0·11	0·6	2·20	0·04	1·0	2·27	0·00
0·3	2·11	0·08	0·7	2·21	0·03			

(b) *Ethyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6	x (EtOH)	EtOH	C_6H_6
0·0	0·00	1·17	0·4	1·54	0·16	0·8	1·60	0·11
0·1	1·45	0·22	0·5	1·55	0·15	0·9	1·65	0·08
0·2	1·51	0·18	0·6	1·56	0·14	1·0	1·77	0·00
0·3	1·53	0·16	0·7	1·58	0·13			

(c) n-*Butyl alcohol–benzene*

	Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:			Adsorption (mmoles/g.) of:	
x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6	x (BuOH)	BuOH	C_6H_6
0·0	0·00	1·17	0·4	1·10	0·31	0·8	1·35	0·11
0·1	1·03	0·36	0·5	1·14	0·28	0·9	1·43	0·05
0·2	1·05	0·34	0·6	1·19	0·24	1·0	1·49	0·00
0·3	1·08	0·32	0·7	1·26	0·18			

adsorption in which the adsorbent showed the greatest preference for one adsorbate (alcohol–benzene systems with "gibbsite"), equation (1) could still be applied. This is a very severe test, for the first layer could be predicted to be very largely composed of alcohol at most concentrations, owing to hydrogen-bonding between the hydroxyl groups of the alcohol and the surface. Thus the only cases in which equation (1) could not be applied directly were those for which evidence of chemisorption was found. The more complex adsorption taking place in these cases can be interpreted in terms of chemisorption of the alcohol, followed by unimolecular physical adsorption on to the new surface so formed.

It is valuable to compare the mole-fraction of ethyl alcohol which is *physically* adsorbed from mixtures with benzene on each of the three solids. The curves are in the order

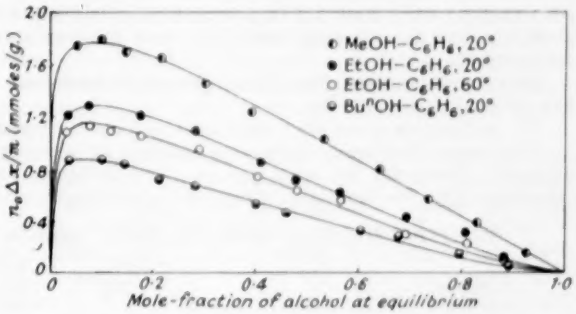


FIG. 9. *Isotherms of concentration change for adsorption on gibbsite-type surfaces from alcohol–benzene systems.*

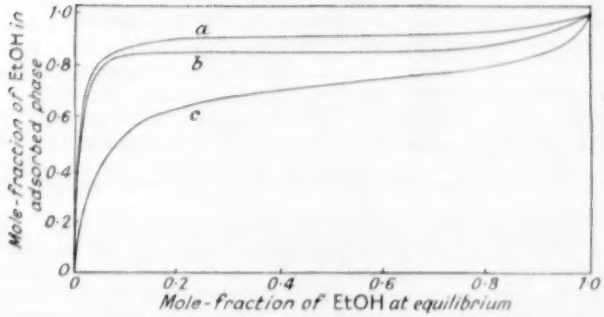


FIG. 10. *Mole-fraction of ethyl alcohol adsorbed from mixtures with benzene on different surfaces: (a) gibbsite-type surface, (b) "ethylated" boehmite, (c) "ethylated" γ-Al_2O_3 (Sample 2).*

required by the above discussion (Fig. 10). The alcohol is most strongly held (relative to benzene) by the completely hydroxylic surface, less strongly by the modified boehmite surface which presents a mixture of hydroxide and alkyl groups, and less strongly still by the modified γ-Al_2O_3 surface, which has a considerably lower proportion of accessible hydroxide groups.

In terms of both physical adsorption and chemisorption, these results suggest that, when an alcohol is being used in chromatography with an alumina column, some thought should be given to the "degree of hydration" of the alumina. This has already been appreciated empirically,[14] but the present studies give a detailed explanation.

Finally we note that Bartell, Scheffler, and Sloan's work on silica gel [4] gave very high maxima in the isotherms of concentration change for systems containing an alcohol, suggesting that chemisorption takes place similarly on this surface. We hope to report on this in a later paper.

[14] Lederer and Lederer, "Chromatography," Elsevier, Amsterdam, 1954.

Experimental

Adsorbents.—The boehmite was Messrs. Peter Spence's "Type A" activated alumina, which the manufacturers state to be essentially sub-crystalline γ-AlO·OH; it was used in B.S.S. grading 6—20. Two samples of anhydrous alumina, γ-Al_2O_3, were made by heating this boehmite (i) to 500° for 5 hr., (ii) to 700° for 24 hr.; the surface areas differed accordingly. The material with the gibbsite-type surface was made by keeping the boehmite under water for 4 weeks at room temperature, and then drying it at about 80°. This procedure was followed because gibbsite cannot be made in bulk with a large surface area. Alkylated aluminas were made by similar treatment of boehmite and anhydrous alumina respectively with the appropriate alcohols; excess of alcohol was removed under vacuum at room temperature.

The charcoal sample was that used by Blackburn and Kipling.[8]

Adsorbates.—The alcohols were treated with magnesium activated by iodine,[15] and fractionated. The fractions used had the following values for n_D^{20}: methyl alcohol, 1·3289 (cf. 1·3291 [16]); ethyl alcohol, 1·3613 (in agreement with Smith and Bonner's value [17]); *n*-propyl alcohol, 1·3854 (in agreement with Carley and Bertelsen's value [18]); *n*-butyl alcohol, 1·3993 (cf. 1·3992 [19]).

Methyl acetate was refluxed over phosphoric oxide and fractionated. The fraction used had n_D^{20} 1·3612 (cf. 1·3619 [20]).

The purification of the other absorbates used has been described previously.[2,3]

Procedure.—Monolayer values were obtained by applying the B.E.T. equation to the 20° adsorption isotherms for each vapour. The isotherms were of Type IV in Brunauer's classification.[21] The monolayer values calculated from them are summarised in Table 5.

Table 5. *Monolayer values from* B.E.T. *equation (in millimoles per g.)*

	$CHCl_3$	$C_2H_4Cl_2$	MeOAc	C_6H_6
Boehmite	1·531	1·481	1·528	1·369
γ-Alumina (1)	—	0·813	—	0·765
	C_6H_6	MeOH	EtOH	Bu^nOH
Boehmite	1·369	—	—	—
"Gibbsite"	1·174	2·274	1·773	1·492
"Methylated" boehmite	1·083	2·124	—	—
"Ethylated" boehmite	0·971	—	1·400	—
"Butylated" boehmite	0·833	—	—	1·081
γ-Alumina (2)	0·854	—	—	—
"Methylated" γ-alumina (2)	0·708	1·494	—	—
"Ethylated" γ-alumina (2)	0·567	—	0·947	—
"Butylated" γ-alumina (2)	0·525	—	—	0·754

Adsorption from the liquid phase has been described previously,[2,3] and took place at 20° except where another temperature is recorded.

In connection with vapour-phase adsorption, we have noted that activated alumina can catalyse the decomposition of ethyl alcohol at low temperatures. Although the recorded rates of decomposition [22] are only small, it seemed desirable to make sure that such decomposition was not responsible for the long time apparently required for equilibrium to be reached in the liquid-phase experiments, the refractive index of the mixture being taken as the criterion. Accordingly, ethyl alcohol was shaken with boehmite for periods up to two weeks and was examined for a change in refractive index. No change was found greater than the experimental error. Although we believe that some catalytic decomposition does take place, we think that it is on too small a scale to modify the conclusions reached above.

We acknowledge with gratitude a grant made to the Department of Chemistry by The Distillers Company Limited. We are also grateful to Peter Spence and Sons Limited for valuable discussions and for the gift of alumina samples.

The University, Hull. [*Received, December 12th*, 1955.]

[15] Weissberger, Proskauer, Riddick, and Toops, "Organic Solvents," Interscience, New York and London, 2nd edn., 1955.
[16] Edwards, *Trans. Faraday Soc.*, 1937, **33**, 1294.
[17] Smith and Bonner, *Analyt. Chem.*, 1952, **24**, 517.
[18] Carley and Bertelsen, *Ind. Eng. Chem.*, 1949, **41**, 2806.
[19] Smyth and Stoops, *J. Amer. Chem. Soc.*, 1929, **51**, 3312.
[20] Vogel, *J.*, 1948, 624.
[21] Brunauer, "Physical Adsorption of Gases and Vapours," Oxford Univ. Press, 1944.
[22] Heinemann, Wert, and McCarter, *Ind. Eng. Chem.*, 1949, **41**, 2928.

945. *Crystal Symmetry, and the Adsorption of Dyes by Growing Crystals. Part I. Ammonium Nitrate IV.*

By JOHN WHETSTONE.

The suitability for dye adsorption of the principal low-index planes of ammonium nitrate IV is discussed in the light of the scheme proposed previously [1] to explain modifications of crystal habit by dyes. The evidence of dye adsorption on certain planes obtained by study of dye inclusions in modified crystals is consistent with the expectations from the above study of the crystal structure.

AMMONIUM NITRATE IV, when crystallised from saturated solutions containing a dissolved dye, frequently gives platy habit-modified crystals with pleochroic coloured regions containing adsorbed dye. Observations from some such crystals have already been used [1] in connection with the derivation of a theory of the mechanisms of crystal-habit modifications. This paper shows how the observed pleochroic inclusions with a variety of dyes of different structures are essentially related to the crystal symmetry of ammonium nitrate IV and the habit modifications produced.

Structure of Ammonium Nitrate IV Crystals.—Ammonium nitrate IV, stable between 32·3° and −18°, usually separates on very careful crystallisation as acicular pseudo-monoclinic {110} needles or prisms, with bipyramidal terminations. Concordant *X*-ray crystallographic determinations of its orthorhombic structure have been described.[2,3]

Planes on which planar dye molecules might preferentially be adsorbed are {100}, {010}, {001}, {101}, and {110}. Dye adsorption on one of the three pinacoidal forms {100}, {010}, and {001} would explain the frequent production of pleochroic dye adsorbates in modified ammonium nitrate IV crystals. The {001} plane consists of layers of ions all of one kind, but alternately regularly displaced by about 0·3 Å perpendicular to {001}. The {010} plane is of high reticular density and contains both ammonium and nitrate ions, all the latter being coplanar. The {100} plane is similar in type, but the nitrate ions are all perpendicular to {100}.

The {110} plane is composed of both anions and cations accurately centred, with the nitrate ions all inclined at about 45° to the plane. The reticular density is high, as also it is in {101} which, too, is composed of alternate anions and cations. These domal and prismatic forms, however, are obviously not suited to the production of pleochroic dye adsorbates.

According to ideas already expressed [1] it may be concluded that {010} is likely to be the pinacoid least suitable for adsorption of planar dye molecules, because the included nitrate ions and the planes of the oxygen triangles of the sulphonate groups of the dye would be mutually orthogonal. It is significant therefore that the most frequent habit modifications observed are on this plane, and {101}, {001}, and {100} are the forms most likely to be concerned in adsorption of dyes.

Adsorption on {110} should also be possible. This is a prismatic form, however, and it is probable that dye adsorption on {110} would merely accentuate the ordinary acicular habit of ammonium nitrate IV, which is not a very distinctive change.

The Possible Dual Nature of Habit Modifications.—A point not previously considered is the opportunity for the simultaneous restriction of growth rates on planes of two forms given by adsorption on planes of a third form. For example, when dye adsorption is on {100} retardation of growth should follow on {010} and {001}, to both of which (100) is an edge plane, and the final habit of the crystal would be an expression of the effect of the dye adsorption on the rates of growth in the *a*, *b*, and *c* directions. Owing to the close similarity of the polar-group spacing of the dye molecule and the ionic pattern of the crystal plane, overgrowth of adsorbed dye molecules on {100} is likely to be relatively easy; thus the rate of growth is likely to be less affected in the *a* than in the *c* direction. However, the

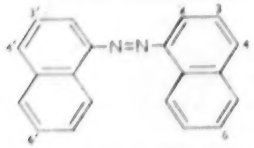
[1] Whetstone, *Trans. Faraday Soc.*, 1955, **51**, 973, 1142.
[2] Hendricks, Posnjak, and Kracek, *J. Amer. Chem. Soc.*, 1932, **54**, 2766.
[3] West, *ibid.*, p. 2256.

habit of the crystals is also influenced by their inherent growth tendencies in these directions. The final habit of the modified crystals is usually found to be more elongated in the *a* than in the *c* direction.

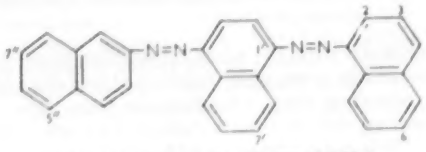
Experimental

Ammonium nitrate was crystallised slowly from slightly supersaturated solution at room temperature or at a constant temperature of 24°.

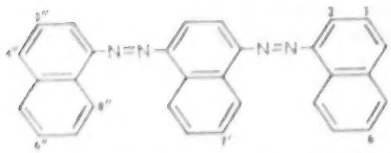
The habit modification on {010} is usually very distinctive, because the modified crystals,



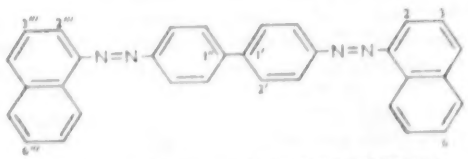
(I) *a*: 2-OH; **3**:**6**:**4′**-$(SO_3Na)_3$
b: 2-NH_2; **3**:**6**:**4′**-$(SO_3Na)_3$
c: 2-OH; **3**:**6**:**3′**:**6′**-$(SO_3Na)_4$



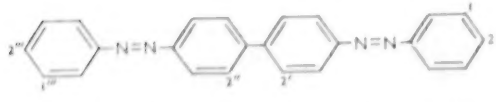
(II): 2-OH; **3**:**6**:**7′**:**5″**:**7‴**-$(SO_3Na)_5$



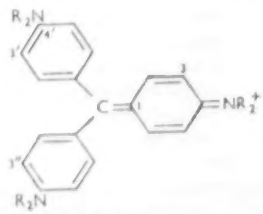
(III) *a*: 2-OH; **3**:**6**:**7′**:**4″**:**6‴**:**8‴**-$(SO_3Na)_6$
b: 2-OH; **3**:**6**:**7′**:**3″**:**6‴**:**8‴**-$(SO_3Na)_6$



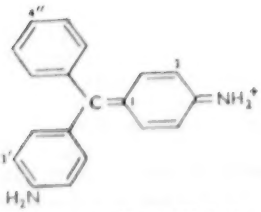
(IV): 2:**2‴**-$(NH_2)_2$; **3**:**6**:**2′**:**3‴**:**6‴**-$(SO_3Na)_5$



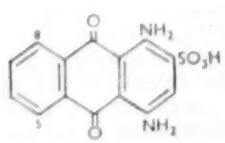
(V): 2:**2‴**-$(OH)_2$; **1**:**1‴**-$(CO_2Na)_2$; **2′**:**2″**-$(SO_3Na)_2$



(VI) *a*: R = H; **3**:**3′**:**3‴**-$(SO_3Na)_3$
b: R = H; **4**(or **4′** or **4″**)-Me; **3**:**3′**:**3‴**-$(SO_3Na)_3$
c: R = H; **4**:**4′**:**4‴**-Me_3; **3**:**3′**:**3‴**-$(SO_3Na)_3$
d: R = Me; **3**:**3′**:**3‴**-$(SO_3Na)_3$



(VII) *a*: **3**:**3′**:**4″**-$(SO_3Na)_3$
b: **3**:**3′**-$(SO_3Na)_2$



(VIII)

lying on a microscope slide, show centred " acute bisectrix " interference figures when viewed conoscopically. For this reason systematic investigation of the relation between the structures of habit-modifying dyes and the crystal planes involved in the dye adsorption has been confined to the {010} habit modifications of ammonium nitrate.

The key to the structures of the dyes is given in the Table.*

Acid Magenta and Related Dyes.—Acid magenta (Imperial Chemical Industries Limited) in concentration 0·2—0·5% by weight in a saturated ammonium nitrate solution below 32° was found readily to induce crystallisation of the salt as soft slimy lamellar aggregates. Other commercial samples of this dye behaved likewise, and also the commercial dye red-violet 5RS (*N*-monoethyl-acid magenta). On reduction of the concentration of dye to 0·01—0·005%, careful crystallisation usually yielded {010} platy or lath-like crystals elongated on {100} with a central rib or " hour glass " of pleochroic dye inclusion along the axis of elongation. Specially prepared dyes which gave similar effects were trisulphon-

Ammonium nitrate IV {010} *Modification. Crystal habit-modifying dyes.*

Structure *	Dye	Plane of adsorption (pleochroism)	(fitting)	Location of polar groups on diagram of plane (X = SO_3^- group)
		Azo-dyes		
Ia	" Amaranth " or BA	{100}	{100}	X(4′)-10 OH(2)-7, X(3)-8, X(6)-3
Ib	D1F	{100}	{100}	X(4′)-10 NH_2(2)-7, X(3)-8, X(6)-3
Ic	α-Naphthylamine-3 : 6-disulphonate → β-naphthol-3 : 6-disulphonate	{001}	{100} or {001}	
II	EJ	{001}	{001}	X(5″)-9, X(7″)-13, X(7′)-15· X(3)-, X(6)-8
IIIa	E2D	{001}	{001}	X(4″)-1, X(6″)-5, X(8″)-6 X(7′)-non-coplanar X(3)-8, X(6)-12*a* (near) †
IIIb	E2E	{001}	{001}	X(3″)-12, X(6″)-15, X(8″)-11 X(7′)-non-coplanar X(3)-2, X(6)-5
IV	" Trypan-red " (C.I. 438)	{100}	{100}	X(3″)-5, X(6″)-2, X(2′)-, X(3)-17, X(6)-21, NH_2-13
V	" Chromazol-yellow CRS " (C.I. 441)	{100}	{100}	X(2′)-7, X(2″)-11, CO_2H(1)-5 CO_2H(1‴)-13
		Triphenylmethane dyes		
VIa	Trisulphonated pararosaniline (C.I. 676)	{100}	{100}	NH_2(4)-11, NH_2(4′)-2, NH_2(4″)-8 X(3)-10, X(3′)-6, X(3″)-8
VIb	Trisulphonated rosaniline (" acid magenta ") (C.I. 692)	{100}	{100}	ditto
VIc	Trisulphonated " new magenta " (" acid magenta ND ") (C.I. 678)	{100}	{100}	ditto
VId	Trisulphonated methyl-violet (C.I. 680)	{100}	{100}	NMe_2(4)-11, NMe_2(4′)-2, $NHMe_2$(4″)-8 X(3)-10, X(3′)-6, X(3″)-12
VIIa	Trisulphonated " Döbner's violet "	{100}	{100}	NH_2(4)-1, NH_2(4′)-10 X(3)-5, X(3′)-9, X(4″)-
VIIb	Disulphonated " Döbner's violet "	{100}	{100}	NH_2(4)-5, NH_2(4′)-7 X(3)-6, X(3′)-7
		Anthraquinone dye		
VIII	1 : 4-Diaminoanthraquinone-2-sulphonate	{100}	{100}	NH_2(1)-7, NH_2(4)-6 X(2)-11

* The structures give the dyes as sodium sulphonates. As there is no generally accepted convention for numbering the ring systems of bisazo(or tetrazo)-compounds, the extreme right-hand systems in the formulæ shown have unprimed numerals, and primes, seconds, etc., are added as necessary as one reads towards the left. Ring systems having fixed numbering (*e.g.* benzidine, salicylic acid) retain that numbering primed as required.

† 12*a* is next anion in line with 12 in Fig. 2.

ated derivatives of the following: (*a*) new magenta (C.I. 678), (*b*) rosaniline (C.I. 677), (*c*) pararosaniline (C.I. 676) (only after modification of the pH to 3—4), and (*d*) methyl-violet (C.I.680) (with difficulty). The leuco-bases of these dyes were not habit-modifiers, presumably because of their non-planar configurations. Attempts to prepare mono- and di-alkylated acid magenta in a pure state were unsuccessful. Trisulphonated rosolic acid only gave very weak modifications of ammonium nitrate IV. These dyes are all characterised by *meta*-sulphonation and *p*-amino-, *p*-alkylamino-, or *p*-hydroxy-groups on each phenyl group of the triphenylmethyl radical.

* Figures in parentheses after names of dyes, *e.g.*, (C.I. 692), give the reference in the Colour Index (F.M. Rowe, Society of Dyers and Colourists, 1924).

FIG. 1. (100) *Plane, with superimposed structure (to same scale) of trisulphonated pararosaniline.* (Plain circles are ammonium ions, double circles represent edgeways view of nitrate ions.)

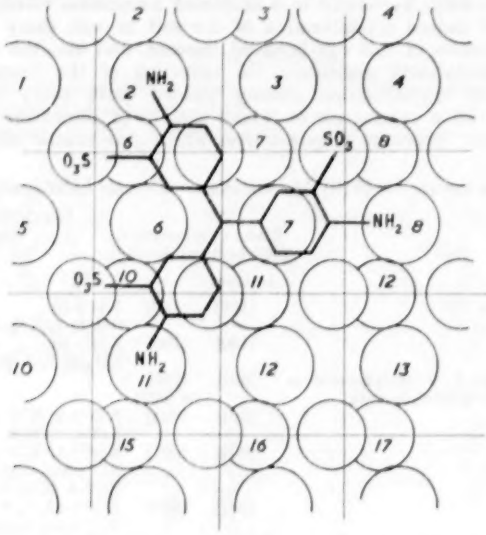
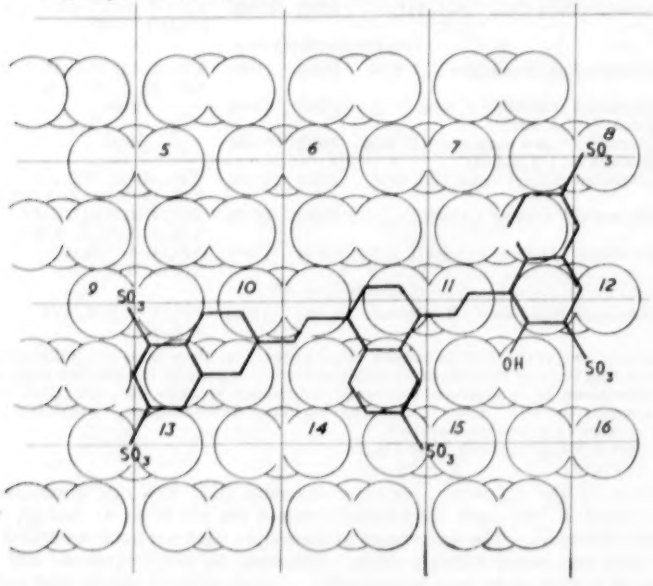


FIG. 2. (001) *Plane, with superimposed structure (to same scale) of dye EJ.* (Nitrate ions are shown edgeways. Unnumbered ions are 0·298 Å above those numbered.)



The optic axial plane {001}, deduced from the orientation of the melatopes of the interference figure, was in all cases parallel to the direction of elongation of the modified crystals, which must therefore be the *a* axis. Examination in polarised light showed that the colour was at a minimum when the electric vector was aligned with the optic axial plane, but it reappeared strongly when the optic axial plane was perpendicular to the electric vector.

Polarisation should be at a maximum when the electric vector is in the plane of the dye molecules, which must therefore be adsorbed on {100} or a plane almost parallel with (100).

Comparison of the acid magenta structure with possible planes for adsorption indicated that excellent agreement of the amino-groups with cation sites could be obtained on {130}; but since sulphonated diamino-triphenylmethane dyes such as trisulphonated Döbner's violet and *mm'*-disulphonated Döbner's violet gave precisely similar modifications to acid magenta, and these dyes could not be considered to be fixed in the lattice merely with two amino-groups replacing ammonium ions, it was most probable that adsorption was actually on {100}. It was possible to accommodate both anionic and cationic groups in ionic sites in this plane, and probably the notably high proportion of polar groups replacing ions in the crystal plane is responsible for the very strong habit-modifying tendencies of this type of dye.

The absence of polar groups on the third phenyl ring improves the fitting of *mm'*-disulphonated Döbner's violet as compared with acid magenta, which is consistent with the powerful habit-modifying effects observed with both the dye and its leuco-base. The reduced effect noted with trisulphonated Döbner's violet is probably connected with the *para*-sulphonation of the third phenyl ring, which results in a misfit between the dye structure and the (100) plane.

Pentasulphonated Aniline-blue.—The commercial sulphonated aniline-blues (C.I. No. 706) are mainly trisulphonates, and had but a slight modifying effect on ammonium nitrate IV. When these products were further sulphonated, in common with ink-blue A.S. prepared by direct sulphonation of aniline-blue, they showed more activity. A laboratory product, appearing from analysis to be slightly more than pentasulphonated, gave modified crystals of ammonium nitrate IV in the shape of thin {010} laths elongated on {100} and containing a central strip of pleochroic dye inclusion. The colour was at a maximum when the electric vector was aligned with the *a* axis. This is indicative of dye adsorption on {001}, which is in harmony with the highly sulphonated character of the dye, since the layers of ions in this plane are all of the one kind.

Amaranth or Naphthol-red S and Related Dyes.—Amaranth, or the pure dye preparation BA, induced the crystallisation of ammonium nitrate IV in soft, red, apparently lamellar masses but on closer examination the individual platy crystals appeared to be parallel aggregates of thin fibre-like crystals. With other isomeric dyes in which the same sulphonate group orientation as in amaranth is retained, *e.g.*, D1F, a similar structure was observed in the crystals of ammonium nitrate IV obtained, although owing to the lessened activity of some of these dyes the constituent fibres of the crystals were coarser. These fibres were oriented in the platy aggregate so as to present their {010} faces in all cases. Cinephotomicrographic observation of their growth process showed that they were formed by an initial parallel growth of fibre-like crystals close side by side followed by a filling in of the intervening spaces.

Microscopic examination of the amaranth-modified crystals showed that the direction of elongation of the constituent fibres was along the *a* axis, and that the fibrous crystals were markedly pleochroic. The colour was at a maximum when the electric vector was parallel with the *c* axis. This implies that the amaranth molecules are located on {100}, if the previous assumption that the dye molecules should be in a plane perpendicular to the habit-modified plane containing the coplanar nitrate ions is accepted.

It is fortunate that this particular instance permits testing of this hypothesis. The amaranth molecule can be fitted on {100} with its sulphonate groups occupying the sites of three nitrate ions. However, the dye can also be fitted flat on to {010}, although the oxygen triangles of the sulphonate groups are then perpendicular to the nitrate ions. The dye molecule when fitted on to {010} lies along the {101} direction. If this in fact represented the true mode of adsorption of amaranth on ammonium nitrate IV, then the maximum colour on rotating the modified crystals in polarised light should be developed when the electric vector is intersecting the fibres at an angle of about 50°, and not as was observed.

The Bis-azo-dye EJ (β-Naphthylamine-5 : 7-disulphonate→α-Naphthylamine-7-sulphonate→β-Naphthol-3 : 6-disulphonate).—The usual crystals of ammonium nitrate IV modified with EJ were quite dissimilar from those modified with amaranth. In place of the parallel growth of fibres, the initial growth of the crystals at fairly high rates appeared as dendrites branching at an acute angle (*ca.* 17°) and the space between the dendrites was then filled in with a platy growth. If the rate of growth of the crystals was slow, the dendritic growth was much less apparent or occasionally not observed, and a crop of thin, soft, lath-like crystals was obtained. A number of these crystals examined possessed a strongly coloured central rib, which was strongly pleochroic. The elongation of the laths was on {100}, and the colour of the crystals was found to be a maximum when the electric vector was parallel with their elongation, from

which the dye molecules must be located on {001}. The dye molecules may be fitted on to ions all at one level in {001}, the only non-fit being the 3-sulphonate group of the R-salt component. A dye E2F (β-naphthylamine-5 : 7-disulphonate→α-naphthylamine-7-sulphonate→β-naphthol-6-sulphonate), prepared to test the effect of omitting this apparently non-useful sulphonate group, was unfortunately almost completely insoluble, but its crystal habit-modifying powers were still apparent, which is indicative of exceptional potency in the very low concentration obtained.

The Bis-azo-dyes E2D and E2E (respectively α-Naphthylamine-4 : 6 : 8- or -3 : 6 : 8-trisulphonate→α-Naphthylamine-7-sulphonate→β-Naphthol-3 : 6-disulphonate).—These dyes gave similar crystals to those modified with EJ. Their characteristics and pleochroism were precisely the same, and the dye molecules could be located on {001} with all sulphonate groups but the central 7-sulphonate of E2E and the central 7-sulphonate and the 6-sulphonate of the R-salt component of E2D, occupying anion sites.

These dyes are examples of those in which the coplanarity of the component naphthalene ring systems is sterically hindered by the 8-sulphonation of the first coupling component. The strain in the molecules may be relieved if the central coupling component is forced out of coplanarity by the 8-sulphonate group; this, however, will still allow coplanarity of the first and the third naphthalene ring system to be maintained. Since the 7-sulphonate of the central α-naphthylamine component apparently does not assist in the dye adsorption when all the rings are forced into coplanarity, this would not appear to be a factor capable of materially altering the adsorptive forces between the crystal lattice and the other polar groups of the dye molecules.

The Aminoanthraquinonesulphonic Acids.—1 : 4 : 5 : 8-Tetra-aminoanthraquinone can be fitted accurately on to the modified plane {010} of ammonium nitrate IV, but this insoluble compound could not be expected to exert any effect on crystal habit. When sulphonated it became only slightly soluble, and modified ammonium nitrate IV crystals to laths on very slow crystallisation above pH 8, but this modification may also be explained by dye adsorption on {100}.

Sodium 1 : 4-diaminoanthraquinone-2-sulphonate was quite soluble and had a marked habit-modifying power for ammonium nitrate IV, platy {010} crystals often being obtained. On careful crystallisation, thin elongated plates with a central rib of pleochroic dye inclusion could be obtained, or sometimes with " hour-glass " inclusions. On examination in polarised light, it was found that the maximum colour was produced when the electric vector was perpendicular to the *a* axis. This indicates that the dye molecules must lie on {100}, and indeed it is possible to locate the two amino-groups on cation sites and the sulphonate group on an anion of {100}.

Chromazol-yellow C.R.S. (C.I. 441).—This dye, although only slightly soluble, was nevertheless capable of bringing about platy development of ammonium nitrate IV under favourable conditions of crystallisation. These thin {010} crystals obtained in the presence of the dye appeared almost completely colourless; but it was possible by less careful control of temperature on some occasions to obtain lath-like crystals of ammonium nitrate, with a central rib of adsorbed dye which was sufficiently conspicuous to allow observation of its colour changes in polarised light as the crystal was rotated. The pleochroism was identical with that of the previous example, so that dye adsorption must be on {100}; and, in fact, it is possible to fit the dye molecule in {100}, with its two carboxyl groups and its two sulphonate groups quite accurately replacing nitrate ions (disregarding any departure from coplanarity of the benzidine portion) and one hydroxy-group occupying an ammonium ion's site.

Cinephotomicrographic Study of Growth of Modified Ammonium Nitrate Crystals.—Cinephotomicrographic study of the growth of crystals of ammonium nitrate modified with acid magenta (0·2% in the saturated salt solution) showed clearly that their soft, slimy nature was due to dendritic growth processes.[4] The dendritic crystals grow strongly in two directions inclined to one another at an acute angle (about 17°). This is consistent with the suppression of the crystals' growth on {100} and {001}, the growth now being most rapid on {101} and {102} which are planes of reasonably high ionic reticular densities, the normals being inclined to one another at 18° (approx.). The extreme complexity and thinness of these dendritically grown crystals is clearly responsible for the effectiveness of surface-coating ammonium nitrate with this dye in preventing the caking of ammonium nitrate in bulk.[5] The same conclusions apply to a number of other crystals habit-modifying dyes.

[4] Whetstone, *Ind. Eng. Chem.*, 1952, **44**, 2663.
[5] Whetstone, B.P. 625,077/1949.

Diagrammatic Illustrations of Adsorbed Dyes on Crystal Planes.—Diagrams of the two pinacoids {100} and {001} most commonly concerned in habit-modification phenomena are reproduced (Figs. 1 and 2), and the dyes acid magenta and EJ respectively are shown superimposed on the planes. In order to facilitate comparisons of other dye structures with these planes the ions are all numbered, and the ionic positions on which the polar groups of the dyes considered may be superimposed are given in the Table. The sulphonate groups of the dyes are depicted merely as carbon–sulphur bonds; it will be understood that the planes of the oxygen triangles of the sulphonate groups are perpendicular to the plane of the dye molecules.

It may be seen from the Table that it is possible to account for many habit modifications in terms of dye adsorptions in conformity with the pleochroism exhibited by the modified crystals, and that there are no apparent exceptions.

The few crystals without pleochroism examined have usually contained only very faint dye inclusions, so that there has been no suspicion of their abnormality. The only modified crystals not falling into line with the {010} platy kind have been fibrous growths obtained with azofuchsine G and one or two other dyes—unfortunately this type of growth has only been observed with one dye of verifiable structure and no conclusions are justifiable from consideration of such an isolated instance.

Interpretations of the plane of adsorption from coloured dye inclusions in crystals have in general been straightforward. The "Trypan-red" dyes are exceptions in that pleochroism was relatively slight with respect to the depth of colour of dye inclusions. Simultaneous adsorption on two pinacoids perpendicular to {010} may account for this. Where only one or two sulphonate groups have been concerned in the habit-modification phenomena, the fitting of models of the dye structure on to the probably concerned crystal planes will often not give a unique solution of the problem of the mode of adsorption of the dye molecules, so that the evidence of dyes containing more polar groups is in general more valuable. Some habit modifiers have not been considered owing to our ignorance of their structures, *e.g.*, sulphonated phthalocyanine which is adsorbed on {001}.

The author acknowledges the aid of Imperial Chemical Industries Limited, Dyestuffs Division, and Dr. E. K. Pierpoint, who prepared many dyes not listed in the Colour Index, and Professor W. Bradley, Dr. C. H. Giles, and Professor Wilson Baker, who gave many samples of obsolete commercial dyes for testing.

Research Department,
Imperial Chemical Industries Limited, Nobel Division,
Stevenston, Ayrshire. [*Received, December 30th*, 1955.]

---

946. *A Polarographic Study of Copper Malonate Complexes.*

By E. Gelles and G. H. Nancollas.

Association of the cupric ion with the malonate anion in aqueous solution at 25° has been studied by polarography over a range of concentrations. Association constants for the reactions $Cu^{2+} + CH_2(CO_2^-)_2 \rightleftharpoons CH_2(CO_2)_2Cu$, and $Cu^{2+} + 2CH_2(CO_2^-)_2 \rightleftharpoons Cu[CH_2(CO_2)_2]_2^{2-}$ have been obtained.

In our recent studies of the association of dicarboxylic acid anions with rare-earth ions, successive association constants for the reaction $M^{3+} + A^{2-} \rightleftharpoons MA^+$, and $MA^+ + A^{2-} \rightleftharpoons MA_2^-$, were derived from potentiometric measurements.[1,2] For bivalent cations, the second stage of the association $MA + A^{2-} \rightleftharpoons MA_2^{2-}$ would be expected to be less favoured by the electrostatic energy term. The first association constant for copper malonate has been obtained from both conductometric and potentiometric measurements;[3] it is of the same order of magnitude as that for lutetium malonate.[2] Potentiometric evidence has been obtained for the formation[4] of MA_2^{2-}. Previous workers[3] failed to observe any displacement in the polarographic half-wave potential for cupric ion in copper malonate solutions, probably owing to insufficient resolution of the potential scale.

[1] Gelles and Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 98.
[2] Gelles and Nancollas, *ibid.*, p. 680.
[3] Peacock and James, *J.*, 1951, 2233.
[4] Riley, *J.*, 1930, 1642.

The polarographic method, where applicable, is particularly suited to the study of successive equilibria, because it provides the most direct evidence on the number of ligands held by the reducible ion. We have found that in the presence of malonate ion the cupric ion is reversibly reduced, the half-wave potential becoming more negative the higher the malonate concentration. The association is sufficiently strong, and the reactions are sufficiently rapid compared with the rate of diffusion of cupric ions to the electrode surface, to give rise to a single, reversible, two-electron wave, and to shifts in half-wave potentials from which the successive association constants can be deduced.

Experimental

" AnalaR " reagents were used where available. Copper nitrate solutions were analysed iodometrically for copper; sodium malonate solutions were prepared from sodium hydroxide and malonic acid solutions of known concentration. Gelatin solutions were freshly prepared before use from " Polaritan " material. Potassium nitrate was used as supporting electrolyte.

Measurements were made with a Tinsley pen recording polarograph and dropping-mercury electrode. It was found possible to determine potentials to ± 1 mv by decreasing the voltage span of the instrument from 3·0 to 0·3 volt. A Tinsley potentiometer reading to 0·1 mv was used to check the applied potential and, in conjunction with a standard resistance, the current at various points along the wave. Current values were taken from the envelope of the tops of the fluctuations of the recorder, operated without damping. For a given copper concentration, $i_d/2$ values were constant to within 0·1 μA. With a cell resistance of 1800 ohms, the effect of iR drop on half-wave potentials was negligible. The capillary was made from marine barometer tubing : the drop time was $3{\cdot}6 \pm 0{\cdot}1$ sec., and the mass rate of flow, 1·41 mg. sec.$^{-1}$, was measured on open circuit in 1·0M-potassium nitrate. The polarographic cell was a 20-ml. " Pyrex " vessel provided with a " Quickfit " neck into which the capillary could be lowered. The vessel was also provided with three side arms : one led to a small cup sealed into the base of the cell to collect the dropping mercury, another was fitted with a small bubbler to prevent back diffusion of oxygen, and the third allowed nitrogen to be passed through the cell, after which it served as a connection to the saturated calomel reference electrode through a saturated potassium chloride agar salt bridge. Nitrogen, freed from oxygen by means of vanadium sulphate solution, was bubbled through the cell for 15 min. before each polarogram was recorded. 0·005% of gelatin was used as a maximum suppressor. All measurements were made at $25° \pm 0{\cdot}1°$.

Results and Discussion

In solutions containing cupric and potassium nitrate, a reversible two-electron wave was observed at ionic strengths of 0·1 and 1·0 with a half-wave potential $E_{\frac{1}{2}}' = 0{\cdot}017$ v, relative to the saturated calomel electrode.

Half-wave potentials were obtained from the intercept of the plot of $\log_{10} i/(i_d - i)$ against applied voltage, where i is the current corresponding to the particular voltage and i_d is the diffusion current, corrected for residual current. The equation for the wave

$$E = E^{\frac{1}{2}} - (RT/nF) \ln [i/(i_d - i)] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

requires for a reversible two-electron reduction that the linear plot shall have a slope of 0·0296 at 25°. Reversibility in a typical experiment is illustrated in Fig. 1; the half-wave potential obtained from the intercept is −0·081 v and the slope is 0·030.

The polarographic behaviour of solutions containing a large excess of malonate ion is summarised in Table 1. C_A represents the total malonic acid concentration, C_M the total metal-ion concentration, and $[A^{2-}]$ the malonate-ion concentration in moles/l.

Table 1. *Measurements at high concentrations of malonate ion.*

(Ionic strength = 1)

$10^3 C_A$	$10^4 C_M$	$10^3[Na^+]$	Slope	$E_{\frac{1}{2}}$	$10^3[A^{2-}]$
5·00	3·49	10·00	0·031	−0·126	5·00
2·00	3·49	3·66	0·030	−0·098	1·66
2·00	3·49	3·50	0·029	−0·096	1·50
2·00	3·49	2·80	0·031	−0·083	0·80
1·00	3·49	1·83	0·030	−0·081	0·83

With the malonate ion in large excess, the concentrations of the free malonate ion in solution and on the surface of the mercury drops may be assumed to be equal. The shift in half-wave potential is then given by

$$\Delta E = E_{\frac{1}{2}} - E_{\frac{1}{2}}' = -(RT/nF) \ln K_2 - (xRT/nF) \ln [A^{2-}] \quad . \quad . \quad . \quad (2)$$

where n is the number of electrons involved in the reduction process, x is the number of malonate ions associated with each cupric ion, and K_2 the association constant for the formation of the complex MA_2^{2-} from the cupric ion, activity coefficients being neglected.

The linear relation between ΔE and $\log_{10}[A^{2-}]$ is illustrated in Fig. 2. The slope of the line is 0·058, showing unequivocally that the complex in these solutions is preponderantly CuA_2^{2-}. From the intercept, the association constant at ionic strength $I = 1$ is derived,

$$K_2 = [CuA_2^{2-}]/([Cu^{2+}][A^{2-}]^2) = 2{\cdot}7 \times 10^7 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

At much lower concentrations of malonate ion, eqn. (2) is not applicable since the concentrations of the malonate ion in solution and on the surface of the mercury drop

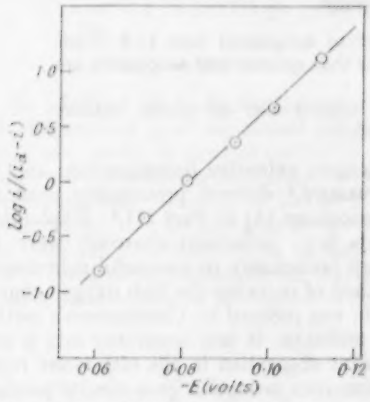


FIG. 1. *Reversibility of reduction for last experiment in Table* 1.

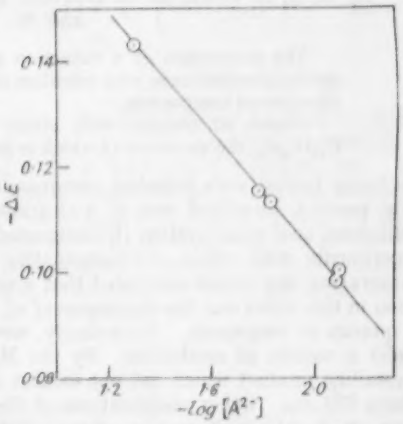


FIG. 2. *Shift in half-wave potential with concentration of malonate ion.*

are not equal. The concentrations at the drop surface, $[M^{2-}{}_0]$ and $[A^{2-}{}_0]$, and the association constants K_1 and K_2, can be calculated from equations (4)—(6).[5]

$$\Delta E = -(RT/nF) \ln (C_M/2[M^{2+}{}_0]) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\Delta E = -(RT/nF) \ln (1 + K_1[A^{2-}{}_0] + K_2[A^{2-}]^2) \quad . \quad . \quad . \quad . \quad (5)$$

$$C_A = [A^{2-}{}_0] + [M^{2+}{}_0](K_1[A^{2-}{}_0] + 2K_2[A^{2-}{}_0]^2) \quad . \quad . \quad . \quad . \quad (6)$$

The relevant data are summarised in Table 2.

TABLE 2. *Measurements at low concentrations of malonate ion.*

(Ionic strength = 0·1)

10^4C_A	10^4C_M	$E_{\frac{1}{2}}$	$10^6[M^{2+}{}_0]$	$10^6[A^{2-}{}_0]$		$10^{-6}K_1$	$10^{-7}K_2$
10·00	4·40	−0·038	3·03	7·00		0·64	5·4
8·00	4·40	−0·033	4·49	5·22		0·65	5·2
6·00	4·40	−0·027	7·14	3·36		0·68	6·0
5·00	4·40	−0·022	10·57	2·52		0·64	5·8
4·00	4·40	−0·017	15·6	1·73		0·67	5·9
2·00	4·40	0·001	63·4	0·38		0·63	5·0
					Mean	0·65	5·4

[5] Ringbom and Eriksson, *Acta Chem. Scand.*, 1953, **7**, 1105.
[6] Davies, *J.*, 1938, 2093.

An approximate thermodynamic association constant K_1° may be calculated from the above value of K_1 at ionic strength 0·1, by using activity coefficients obtained from the Davies equation: [6]

$$K_1^\circ = \{CuA\}/(\{Cu^{2+}\}\{A^{2-}\}) = 5{\cdot}0 \times 10^5 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The polarographic value is in good agreement with the potentiometric ($6{\cdot}9 \times 10^5$) and conductometric ($5{\cdot}6 \times 10^5$) values.[3] The difference between the values of K_2 at ionic strengths 0·1 and 1·0 is presumably accounted for by the change in value of the activity coefficient. At an ionic strength of approximately 0·3, Riley's potentiometric measurements [4] gave a value for K_2 of 3×10^7.

Chemistry Department, The University, Glasgow, W.2. [*Received, April 30th*, 1956.]

---

947. *Quassin and* neo*Quassin. Part V.**

By R. J. S. Beer, B. G. Dutton, D. B. Jaquiss, Alexander Robertson, and W. E. Savige.

The conversion of a reduction product of *neo*quassin into 1 : 2 : 8-trimethylphenanthrene with selenium suggests that quassin and *neo*quassin are diterpenoid compounds.

Fusion of quassin with alkali gives creosol and an acidic lactone, $C_{13}H_{14}O_4$, the structure of which is discussed.

On being heated with selenium, *neo*quassin undergoes extensive decomposition and the only product identified was 3 : 4 : 5-trimethylguaiacol,[1] derived presumably from the α-diketone enol ether system (I) designated chromophore (A) in Part III.[2] Exploratory experiments with other dehydrogenating agents (*e.g.*, palladised charcoal) were not encouraging and it was concluded that a necessary preliminary to successful dehydrogenation in this series was the development of a method of reducing the high oxygen content of quassin or *neo*quassin. Accordingly, *neo*quassin was reduced by Clemmensen's method under a variety of conditions. By the Martin technique it was converted into a non-crystalline product which did not exhibit significant absorption in the ultraviolet region above 220 mμ. Other modifications of the Clemmensen reduction gave similar products from which only small amounts of two crystalline compounds were isolated. Of these, one is apparently a tetrahydronor*neo*quassin, $C_{20}H_{29}O_5{\cdot}OMe$, the ultraviolet absorption spectrum of which indicated the absence of conjugated carbonyl groups whilst the infrared absorption spectrum had peaks at 3401 cm.$^{-1}$ and at 1721 cm.$^{-1}$, due to a hydroxyl group and (probably) to a *cyclo*hexanone residue, respectively. On the basis of the partial formula (II) for *neo*quassin this product is probably (III).

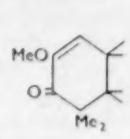
The second crystalline product, $C_{20}H_{29}O_3{\cdot}OMe$, also had no significant absorption in the ultraviolet region (above 220 mμ) and its infrared absorption spectrum did not contain a peak due to a hydroxyl group. The presence of at least one unconjugated carbonyl group in this compound is indicated by the formation of a pale orange 2 : 4-dinitrophenylhydrazone ($\lambda_{max.}$ 370 mμ in alcohol). This reduction product, which is probably formed *via* compound (III), can be tentatively formulated as (IV).

Since neither of the crystalline reduction products of *neo*quassin could be obtained in good yield, it was decided to attempt selenium dehydrogenation of the non-crystalline material from the Martin reduction. The resulting crude dehydrogenation product was separated by distillation into two fractions. On further purification the more volatile fraction gave a colourless oil which is probably an alkylated benzene but which has not been fully characterised. From the high-boiling fraction there was isolated a crystalline hydrocarbon, $C_{17}H_{16}$, which formed well-defined derivatives with picric acid and with

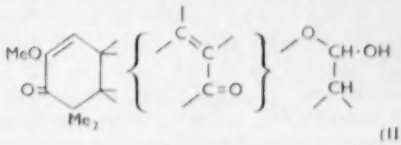
* Part IV, *J.*, 1956, 3280.

[1] Beer, Jaquiss, Robertson, and Savige, *J.*, 1954, 3672.
[2] Hanson, Jaquiss, Lamberton, Robertson, and Savige, *ibid.*, 4238.

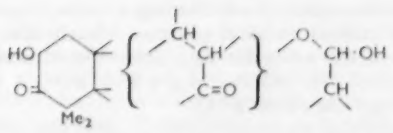
trinitrobenzene, and which from its composition and ultraviolet absorption spectrum [3] appeared to be a trimethylphenanthrene. A survey of the literature suggested 1 : 2 : 8-trimethylphenanthrene [4] (V) and this conclusion was shown to be correct by direct comparison with an authentic sample, kindly supplied by Professor R. D. Haworth, F.R.S.



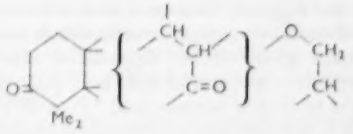
(I)



(II)

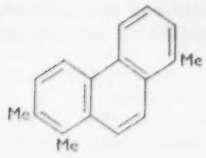


(III)

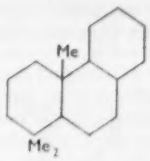


(IV)

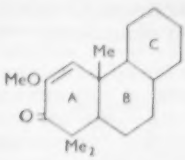
In addition to 1 : 2 : 8-trimethylphenanthrene, the high-boiling fraction from the dehydrogenation gave an almost colourless oil, the ultraviolet absorption spectrum of which was similar in general outline to that of 1 : 2 : 3 : 4-tetrahydrophenanthrene. The orange-red trinitrobenzene derivative melted over a range (73—80°) even after repeated recrystallisation. Analysis of the oil indicated the formulæ $C_{17}H_{22}$ or $C_{17}H_{20}$, the latter corresponding to a tetrahydrotrimethylphenanthrene. In this connexion it is noteworthy that selenium dehydrogenation of dihydroxycassanic acid is reported to yield a mixture of 1 : 2 : 8-trimethylphenanthrene and its tetrahydro-derivative; [5] the latter is a liquid, forming an orange-red trinitrobenzene derivative, m. p. 85—87°.



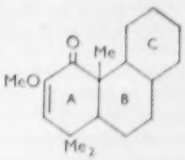
(V)



(VI)



(VII)



(VIII)

The formation of 1 : 2 : 8-trimethylphenanthrene (V) by dehydrogenation of a *neo*-quassin derivative provides the first definite evidence that quassin and *neo*quassin are diterpenoid compounds. The nature of the functional groups and the number of double bonds present being taken into account, it is reasonably certain that quassin contains the carbocyclic system (VI) which is elaborated in partial structures (VII) and (VIII) so as to accommodate the two possible arrangements of chromophore (A). The complete structure for quassin must include: (i) three extra carbon atoms, probably attached to ring C and associated with the lactone system; (ii) a second αβ-unsaturated ketonic system [chromophore B of Part III,[2] possibly sited in ring B]; (iii) a second methoxyl group.

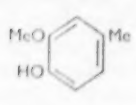
With hot 10% aqueous sodium hydroxide quassin gives a mixture of *allo*quassinolic acid and an isomer,[2] compounds which are evidently stable to the further action of aqueous alkali since they are also obtained when quassin is treated with boiling 50% aqueous sodium hydroxide. Fusion with alkali has now been found to effect extensive degradation

[3] von Heilbronner, Daniker, and Plattner, *Helv. Chim. Acta*, 1949, **32**, 1723; Askew, *J.*, 1935, 509; Barton, Fawcett, and Thomas, *J.*, 1951, 3147.
[4] Haworth and Mavin, *J.*, 1932, 2720.
[5] Ruzicka and Dalma, *Helv. Chim. Acta*, 1939, **22**, 1516.

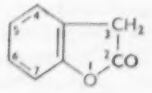
of the quassin molecule and, when carried out in an open vessel, gives rise to small amounts of two well-defined products, one of which was easily recognised as creosol (IX). This guaiacol derivative could arise from ring A in formulæ (VII) and (VIII) or less probably from the ring carrying the second methoxyl group present in quassin. The second product was a monobasic acid, $C_{13}H_{14}O_4$, containing at least two *C*-methyl groups, giving a positive hydroxamic acid test for an ester or lactone group, and forming a monobromo-derivative in which the bromine atom is inert. On methylation with methyl sulphate and alkali, this acid (referred to in the sequel as the C_{13}-acid) was converted into a methoxy-dicarboxylic acid, $C_{13}H_{15}O_4{\cdot}OMe$, which with diazomethane yielded a dimethyl ester, $C_{11}H_{12}(OMe)(CO_2Me)_2$. These results, together with the fact that in alkaline solution the C_{13}-acid couples with phenyldiazonium chloride, support the view that this acid contains a masked phenolic group as part of a lactone system. Our failure to isolate the corresponding hydroxy-acid implies that the lactone system is very readily formed and suggests that the C_{13}-acid may be a derivative of α-coumaranone (X) containing a carboxyl group and four other carbon atoms which must be present as alkyl groups. Clearly the free carboxyl group of the C_{13}-acid is attached to the aromatic ring since the ultraviolet absorption spectrum of this acid ($\lambda_{max.}$ in alcohol 274, 283 mμ; log ε 2·91, 2·90) is very similar to that of benzoic acid [6] ($\lambda_{max.}$ 271, 279 mμ; log ε 2·88, 2·74).

It is not possible at present to assign a particular structure to the C_{13}-acid but certain restrictions can be placed on the arrangement of the substituents. Thus it is unlikely that the carboxyl group occupies the 4-position of (X) because the corresponding methoxy-dicarboxylic acid does not form an anhydride under conditions which bring about anhydride formation with homophthalic acid and similar compounds. The 5-position is probably blocked by an alkyl substituent since the C_{13}-acid gives a negative Gibbs test, in which case the 7-position must be unsubstituted in order to explain the positive coupling reaction. The free carboxyl group is therefore most probably in the 6-position. Bromination of the C_{13}-acid apparently occurs in the 4-position since the bromo-derivative is still capable of coupling with diazonium salts presumably at the 7-position. On the basis of these arguments, it would appear that the C_{13}-acid has a structure of type (XI; R + R′ + R″ = C_4H_{11}).

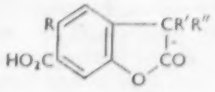
Attempts to clarify this structural problem by oxidative degradation of the methoxy-dicarboxylic acid have been unsuccessful. The fact that with diazomethane in ether and



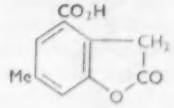
(IX)



(X)



(XI)



(XII)

methanol the C_{13}-acid gave a liquid product with a higher methoxyl content than would correspond to esterification of one carboxyl group was at first thought to indicate that the coumaranone carbonyl group had some enolic character, as suggested by Berner [7] for the lactone (XII). This would imply that at least one hydrogen atom is attached to the β-position of the coumaranone ring, but it was subsequently found that on prolonged treatment with diazomethane the C_{13}-acid was converted into the dimethyl ester of the methoxy-dicarboxylic acid. It is clear therefore that the lactone ring is slowly opened under the conditions employed.

The limited conclusions reached regarding the structure of the C_{13}-acid do not provide a firm basis for a discussion of its relation to quassin. It may well be that the acid is not simply related to the parent molecule. For this reason and because the preparation of the C_{13}-acid involves the destruction of relatively large amounts of quassin, the authors do not at present contemplate any extension of this part of the investigation.

[6] Moser and Kohlenburg, *J.*, 1951, 804.
[7] Berner, *Acta Chem. Scand.*, 1949, **3**, 1117.

Experimental

Unless otherwise stated, the light petroleum used had b. p. 60—80°. Ultraviolet absorption spectra were measured with a Unicam spectrophotometer and infrared absorption spectra with a Grubb–Parsons double-beam spectrometer, a paste of the material in " Nujol " being used.

Reduction of neo*Quassin.*—The amalgamated zinc used in these reductions was prepared by slowly adding a solution of mercuric chloride (0·65 g.) in concentrated hydrochloric acid (1·25 ml.) to an agitated slurry of zinc dust (5 g.) in water (6·5 ml.). After 15 min. the amalgamated zinc was collected, washed with several portions of water, and used immediately.

(*A*) A mixture of *neo*quassin (10 g.), toluene (600 ml.), amalgamated zinc (50 g.), concentrated hydrochloric acid (50 ml.), and water (25 ml.) was vigorously heated under reflux for 70 hr., with additions of more zinc (20 g.) at intervals of 8 hr. and concentrated hydrochloric acid (4 ml.) hourly. The toluene layer was separated, the aqueous liquor extracted several times with chloroform, and the extract combined with a solution obtained by grinding the residual zinc amalgam with chloroform. The concentrated chloroform (15 ml.) and the toluene solutions were combined, washed with successive portions of 2N-aqueous sodium hydroxide and finally with water, dried, and evaporated, giving a yellow gum (8·18 g.) which did not exhibit significant absorption in the ultraviolet region above 220 mμ.

(*B*) A solution of *neo*quassin (1 g.) in methanol (30 ml.) was added to amalgamated zinc (10 g.) and concentrated hydrochloric acid (5 ml.), and the mixture heated under reflux for 36 hr., with the addition of more zinc (4 g. at 7-hourly intervals) and concentrated hydrochloric acid (3 ml. at 2-hourly intervals). The residual amalgam was ground with several portions of chloroform and the solution combined with the chloroform extract of the reaction mixture. Evaporation of the washed (as in method *A*), dried extracts gave an almost colourless gum (0·79 g.), a solution of which in benzene–light petroleum (2 : 3) was passed through alumina. Triturated with light petroleum, the gum (0·56 g.) from the eluate solidified and was repeatedly crystallised from this solvent, giving a *product* in needles, m. p. 160—163°, after sintering at 158° (Found, in a sample dried at 60° for 4 hr. : C, 72·5; H, 9·4; OMe, 8·9. $C_{20}H_{28}O_5$·OMe requires C, 72·4; H, 9·25; OMe, 8·9%). The 2 : 4-dinitrophenylhydrazone separated from chloroform in orange feathery needles, m. p. 272—275°, $\lambda_{max.}$ 370 mμ.

(*C*) A mixture of concentrated hydrochloric acid (5 ml.), amalgamated zinc (20 g.), *neo*quassin (1 g.), and acetic acid (10 ml.) was kept at room temperature for 17 hr., the liquid was decanted, and the amalgam washed with dilute acetic acid. The combined acidic liquors were treated gradually with 5N-aqueous potassium hydroxide (67 ml.) followed by water (50 ml.), heated to 80° for 1 min., cooled, filtered (the pH was 9), and extracted with chloroform. Evaporation of this extract left a gum (0·29 g.) which was dissolved in the minimum amount of ethyl acetate; the gradual addition of light petroleum to this solution gave *tetrahydronorneoquassin* which was repeatedly recrystallised from ethyl acetate–light petroleum forming needles, m. p. 232—233°, after sintering at 227°, with a negative ferric or tetranitromethane reaction (Found, in a sample dried in a vacuum at 120° for 14 hr. : C, 66·85; H, 8·7; OMe, 8·4. $C_{20}H_{28}O_5$·OMe requires C, 66·3; H, 8·5; OMe, 8·2%). This compound was insoluble in 2N-aqueous sodium hydroxide and stable to neutral permanganate solution.

When the reaction mixture obtained at room temperature (Method *C*) was boiled for 16 hr. with the addition of more concentrated hydrochloric acid (5 ml. at 4-hourly intervals) the sole crystalline product isolated after chromatographic purification was identical with the product, m. p. and mixed m. p. 160—163°, obtained by Method (*B*) (Found, in a sample dried *in vacuo* at 80° for 10 hr. : C, 72·2; H, 9·5%).

1 : 2 : 8-*Trimethylphenanthrene.*—The gum (8·18 g.) from method (*A*) was warmed and intimately mixed with powdered selenium (16·3 g.), and the mixture kept at 320—340° for 36 hr. The sticky reaction mixture was triturated with hot light petroleum and then extracted with this solvent in a Soxhlet apparatus for 15 hr. After removal of a little brown, non-crystalline acidic material with 2N-aqueous sodium hydroxide, evaporation of the light petroleum extract left a viscous red oil (3·64 g.) which was distilled, giving three fractions: (i) b. p. 80—100°/0·05 mm. (2—3 drops), (ii) b. p. 160—230°/0·025 mm. (2·23 g.), and (iii) b. p. 230—300°/0·025 mm. (trace). Redistillation of fraction (ii) gave a mixture of oil and crystals, from which the oil was removed with a small pipette. After being washed with a little light petroleum, the residual crystals (110 mg.), m. p. 118—124°, were combined with similar material from another dehydrogenation experiment on 3·9 g. of gum and purified by chromatography on alumina. Elution with light petroleum gave a solid (100 mg.) which on repeated purification

from alcohol afforded 1 : 2 : 8-trimethylphenanthrene in plates, m. p. and mixed m. p. 144—145° (Haworth and Mavin record [4] m. p. 146°); light absorption in 95% ethanol; $\lambda_{max.}$ in mμ (log ε) values as follows: 214 (4·68), 254·5 (4·68), 262 (4·78), 284 (4·10), 295 (4·10), 308 (4·19), 324 (2·62), 340 (2·54), 356 (2·13); $\lambda_{min.}$ in mμ (log ε) as follows: 234 (4·09), 257 (4·67), 280 (4·02), 290 (3·92), 301 (3·83), 321·5 (2·61), 334 (2·39), 354 (2·05); points of inflection: 225 (4·40), 345 (2·32), 349 (2·24) (Found: C, 93·0; H, 7·5. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). Prepared in alcohol, the picrate formed orange needles, m. p. 165—166° (Found: C, 61·4; H, 4·0; N, 9·3. Calc. for $C_{17}H_{16},C_6H_3O_7N_3$: C, 61·5; H, 4·3; N, 9·35%). Haworth and Mavin record [4] m. p. 163° for 1 : 2 : 8-trimethylphenanthrene picrate. The *trinitrobenzene derivative* separated from alcohol in long yellow needles, m. p. 190—191° (Found: C, 63·9; H, 4·1; N, 9·8. $C_{17}H_{16},C_6H_3O_6N_3$ requires C, 63·7; H, 4·4; N, 9·7%).

The oil accompanying the crystalline phenanthrene was purified by chromatography from light petroleum on alumina and eluted with the same solvent, leaving the more strongly absorbed 1 : 2 : 8-trimethylphenanthrene (90 mg.) on the column. Distillation then gave as the main fraction a pale yellow oil (0·16 g.), which on being twice distilled afforded an almost colourless oil, b. p. 160—170°/0·025 mm.; light absorption in 95% ethanol; $\lambda_{max.}$ values in mμ (log ε) 232 (4·67), 286 (3·51), 330 (2·78); $\lambda_{min.}$ in mμ (log ε), 251 (3·18), 324 (2·63); inflection, 314 (2·90) (Found: C, 90·3, 90·35; H, 9·4, 9·6. $C_{17}H_{20}$ requires C, 91·0; H, 9·0. $C_{17}H_{22}$ requires C, 90·2; H, 9·8%). Prepared in alcohol, the trinitrobenzene derivative formed orange-red warts which even after repeated purification had indefinite m. p. (73—80°).

Decomposition of Quassin with Alkali.—A mixture of quassin (20 g.), methanol (40 ml.), and a solution of potassium hydroxide (26 g.) and sodium hydroxide (38 g.) in water (60 ml.) was heated in a nickel crucible, at first on the steam-bath (until most of the methanol had evaporated) and subsequently in a metal bath, the temperature of which was raised to 240° during 1 hr. and then kept at 240—260° for 15 min. A solution of the reaction mixture in water (500 ml.) was saturated with carbon dioxide, and the phenolic product isolated by continuous extraction with ether. On distillation this gave an oil, b. p. *ca.* 130°/2 mm., with a strong guaiacol-like odour and a greenish-blue ferric reaction. With phenyl *iso*cyanate in light petroleum (b. p. 80—100°), this substance gave the *carbanilate* of creosol which crystallised from light petroleum, containing a little benzene, in needles, m. p. 139—140° (Found: C, 69·8; H, 5·9; N, 5·5; OMe, 12·0. $C_{14}H_{13}O_2N$·OMe requires C, 70·0; H, 5·8; N, 5·5; OMe, 12·1%). This compound was identified by comparison with a specimen, m. p. 139—140°, from authentic creosol (5-methylguaiacol) (Found: N, 5·5; OMe, 11·9%).

After removal of the phenolic fraction the aqueous liquors were acidified with hydrochloric acid and the continuous ether-extraction process repeated, giving a black tarry acidic fraction. Repeated extraction of this product with hot light petroleum, containing a little ethyl acetate, gave a pale yellow gum which on trituration with a little cold ethyl acetate furnished an *acid* (1·85 g.), m. p. 204—208°. Purified by recrystallisation and then by sublimation [160—180° (bath temp.)/0·002 mm.], this compound, the C_{13} "*acid*," had m. p. 212—214° [Found: C, 66·6, 66·8; H, 6·0, 5·9; *C*-Me, 10·5%; *M* (Rast), 212. $C_{13}H_{14}O_4$ requires C, 66·7; H, 6·0%; *M*, 234]. The acid gave a positive hydroxamic acid test for an ester or lactone and coupled in alkaline solution with diazotised aniline but did not give a coloration with 2 : 6-dichloroquinone chloroimide. Attempts to decarboxylate the acid, *e.g.* by the glycerol–copper bronze method, were unsuccessful.

Methylation of the C_{13} *Acid.*—Methyl sulphate (4 ml.) was added portionwise in 30 min. to an agitated solution of the C_{13}-acid (0·6 g.) in 2N-aqueous sodium hydroxide and, after the addition of more aqueous sodium hydroxide (10 ml.), the mixture was heated on the steam-bath for 2 hr. From the cooled, acidified solution the *methyl ether* (0·6 g.) was isolated by extraction with ether and with ethyl acetate and crystallised from ethyl acetate–light petroleum, forming irregular prisms, m. p. 212—214°; the analytical sample, prepared by sublimation, had the same m. p. (Found: C, 63·1; H, 6·9; OMe, 11·7; *C*-Me, 15·0. $C_{13}H_{14}O_4$·OMe requires C, 63·2; H, 6·8; OMe, 11·7%). This methyl ether reacted with sodium hydrogen carbonate did not couple in alkaline solution with diazotised aniline, and was recovered in good yield from an attempted decarboxylation at 250° in glycerol containing copper bronze. With ethereal diazomethane containing a little methanol this compound was slowly converted into a *dimethyl ester*, which was purified by distillation (b. p. 192—202°/0·05 mm.), and then by crystallisation from ether–light petroleum (b. p. 40—60°), forming stout needles, m. p. 72° [Found: C, 65·2; H, 7·7; OMe, 31·7. $C_{13}H_{12}O_2(OMe)_2$ requires C, 65·3; H, 7·5; OMe, 31·6%]. The same ester, m. p. and mixed m. p. 72°, was obtained in low yield by prolonged treatment (*ca.* 20 days) of the C_{13}-acid with excess of ethereal methanolic diazomethane at 0° (Found: OMe, 31·6; *C*-Me, 10·5%).

Bromination of the C_{12} *Acid.*—A solution of the C_{12}-acid (0·2 g.) in acetic acid (2 ml.), containing bromine (0·6 g.) and a trace of iodine, was kept in the dark for 18 hr., and then diluted with water. The precipitated *bromo-derivative* (0·18 g.), m. p. *ca.* 195°, separated from aqueous alcohol and then from ethyl acetate–light petroleum, in rectangular plates, m. p. 201—202° (Found: C, 49·8; H, 4·3; *C*-Me, 11·5. $C_{13}H_{13}O_4Br$ requires C, 49·9; H, 4·2%). This product was recovered in good yield after being heated with 10% aqueous potassium hydroxide for 2 hr.

UNIVERSITY OF LIVERPOOL. [*Received, July 23rd,* 1956.]

948. *The Structure of Molecular Compounds. Part XI.* Crystal Structure of the Addition Complex of Quinol and Methyl Cyanide.*

By S. C. WALLWORK and H. M. POWELL.

The molecular compound $3C_6H_4(OH)_2,M$ ($M = CH_3{\cdot}CN$) has a hexagonal structure closely related to that of the other members of the series ($M = SO_2$, A, etc.) but the β-quinol framework which encloses M is distorted more than in any other known member of the series. This distortion probably includes both slight extension and puckering of the hexagon of hydrogen bonds through which the quinol molecules are linked, and a minor departure from the rhombohedral lattice.

IN Part VI [1] a survey was made of the crystal structures of the series of clathrate compounds of general formula $3C_6H_4(OH)_2,M$, where M is a molecule of dimensions which permit its enclosure in cavities between two interpenetrating giant molecules formed by quinol molecules linked through hexagons of hydrogen bonds. In the structure where M is methyl cyanide the cagework of quinol molecules was considered to be extended to its limit, since the compound decomposed noticeably in the open and methyl cyanide was the largest molecule observed to form this type of clathrate compound. The extension of the cage could be measured by the angle of tilt θ (Fig. 1) of each quinol molecule from the plane of the hydrogen-bond hexagon [which is also the (0001) plane of the hexagonal unit cell in each case]. On the assumption that the hydrogen bonds were of length 2·75 Å in

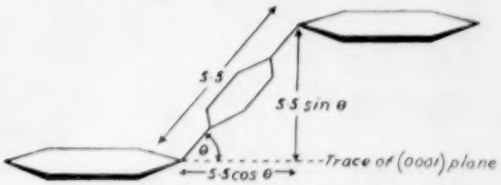


FIG. 1. *One quinol molecule is shown with its oxygen–oxygen axis inclined at an angle θ to the* (0001) *plane, together with two hexagons of hydrogen bonds parallel to this plane. Distances in* Å.

each structure it was possible to calculate the angle θ independently from the *a* and *c* unit-cell dimensions, and in every case but that of the methyl cyanide compound the two values of θ so obtained were in agreement. For the methyl cyanide compound, however, θ was 47° 36′ when calculated from *a* and 49° 10′ when calculated from *c*, and this discrepancy was interpreted as indicating further distortion of the quinol cage either by extension or by puckering of the hydrogen-bond hexagons. In order to investigate this matter further, a more detailed crystallographic study has been carried out.

Crystals were obtained as colourless hexagonal prisms or rhombohedra by cooling warm saturated solutions of quinol in methyl cyanide. By the liquid-air method they gave a weak pyroelectric effect. On exposure to air the crystals lost methyl cyanide and by successive weighings of a sample it was found that half of the total methyl cyanide content was lost after 2½ days and three-quarters after 11 days. *X*-Ray photography of an originally single crystal of the compound showed powder lines of α-quinol appearing superposed on the single-crystal diffraction pattern as the crystal decomposed. Crystals

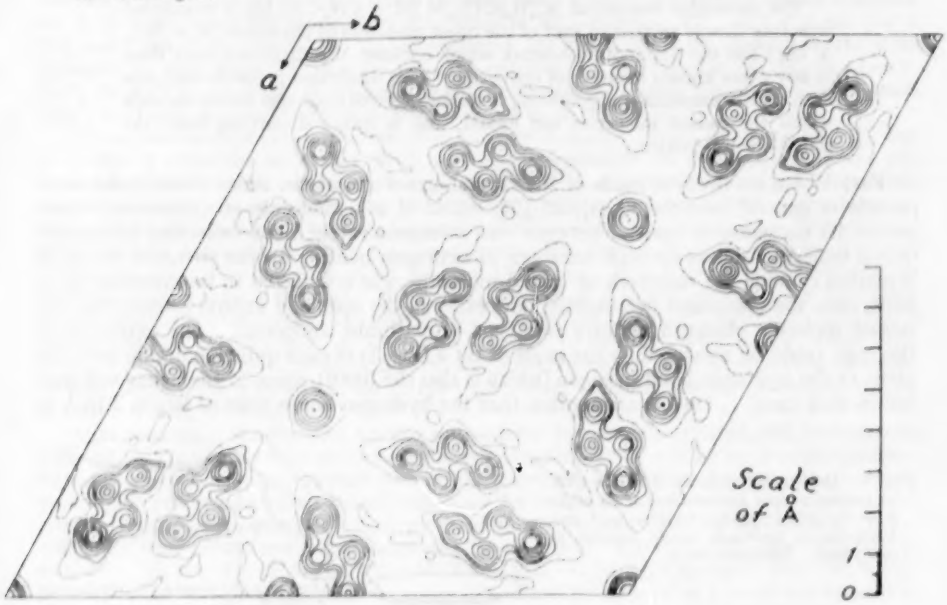
* Part X, *J.*, 1952, 319.

[1] Palin and Powell, *J.*, 1948, 815.

to be used for intensity measurements were protected by coating them with Canada balsam and these showed only slight effects of decomposition after several days. The decomposition interfered with the determination of the density by flotation in xylene–bromobenzene mixtures, but rapid determinations with fresh crystals gave approximately 1·34 g./c.c.

From oscillation and Weissenberg photographs taken with copper radiation, and with the crystal oscillating about the *a* and *c* axes of the hexagonal unit cell, the dimensions were found to be $a = 16{\cdot}01 \pm 0{\cdot}02$, $c = 6{\cdot}25 \pm 0{\cdot}01$ Å. The density, 1·34 g./c.c., and these

FIG. 2. *Electron density projected on* (0001). *Lowest contour at 2 electrons/Å², others at intervals of 1 electron except in the methyl cyanide peaks which have contours at intervals of 2 electrons/Å². The circular peaks represent* $CH_3{\cdot}CN$ *molecules with their linear axes perpendicular to* (0001). *Each of these is surrounded by six groups of peaks representing the quinol cage. There are eight peaks in each group corresponding to the eight atoms of a quinol molecule which is tilted out of the* (0001) *plane as shown in Fig.* 1.



dimensions give for the cell contents 3·02 ≃ 3 units of formula $3C_6H_6O_2{\cdot}CH_3{\cdot}CN$. Intensities were estimated visually on long- and short-exposure Weissenberg photographs obtained by the multiple-film method.

The diffraction patterns obtained resemble those given by the other members of the series, but differ in having some reflections for which $h - k + l \neq 3n$. These reflections are extremely weak and show that, although the structure, unlike the others, cannot as a whole be based on a rhombohedral lattice, the deviation from this is very slight. There are no systematic absences, and the symmetry of the diffraction pattern combined with the non-centrosymmetric character indicated by the pyroelectric effect show that the space group is C3.

If it is assumed that the quinol cagework has almost the same form as in the other structures of the series, and that the lack of a centre of symmetry is due only to the presence of non-centrosymmetric methyl cyanide molecules, Fourier refinement of the structure may be attempted by giving positive or negative signs rather than phase angles to F_{hk0} because the methyl cyanide molecules are seen end-on in projection along the *c* axis. A

similar procedure had proved successful for the methanol compound.[2] Many signs were found by the isomorphous replacement method on the assumption that the differences in intensity of corresponding reflections in the methanol, sulphur dioxide, and methyl cyanide compounds are due mainly to the different scattering powers of the enclosed molecules (*i.e.*, the effect of distortion of the quinol cagework was neglected). In cases where no corresponding reflections had been observed for the other compounds, signs were computed from approximate parameters estimated for the atoms in the structure. In this way signs for all the *hki*0 structure factors having $h - k = 3n$ were determined and corrected by refinement of the Fourier projection on (0001).

In this projection the distortion of the structure from rhombohedral symmetry must be very slight because prolonged exposures show only five reflections having $h - k \neq 3n$. No matter what signs were assumed for these the distortion from rhombohedral symmetry of the Fourier projection was too small to be measured. In the final projection shown in Fig. 2 their signs were adjusted in such a way as to lead to equal electron densities at the positions of the methyl cyanide molecules and to the best correspondence of peak heights for similar atoms in the quinol molecules. Because the distortion from rhombohedral symmetry is too small to be measurable the atomic co-ordinates obtained from this projection and given in the Table still correspond to rhombohedral symmetry, though the co-ordinates of the full asymmetric unit of the hexagonal C3 cell are given.

The atomic positions are not expected to be more accurate than about ±0·05 Å, partly because they are all based on two-dimensional information and partly because of the difficulty of obtaining accurate intensities from crystals subject to decomposition. In view of this, although the projection is most directly interpreted as implying that the hydrogen-bond hexagons are puckered, it is not possible to rule out the alternative mode of distortion of the cagework in which the hexagons are extended but not puckered. The co-ordinates directly observed (Table) correspond to a projected hydrogen-bond length of 2·78 Å and a

Atomic x and y parameters for one asymmetric unit of the cell.

Atom	*x*	*y*	Atom	*x*	*y*	Atom	*x*	*y*
Quinol								
O_1 (OH)	0·090	0·200	C_3 (CH)	0·070	0·262	C_{11} (CH)	0·775	0·662
O_2 (OH)	0·243	0·467	C_4 (C)	0·205	0·401	C_{12} (CH)	0·930	0·738
O_3 (OH)	0·133	0·557	C_5 (CH)	0·108	0·329	C_{13} (C)	0·795	0·599
O_4 (OH)	0·910	0·800	C_6 (CH)	0·263	0·405	C_{14} (CH)	0·892	0·671
O_5 (OH)	0·757	0·533	C_7 (C)	0·067	0·529	C_{15} (CH)	0·737	0·595
O_6 (OH)	0·867	0·443	C_8 (CH)	0·995	0·554	C_{16} (C)	0·933	0·471
C_1 (C)	0·128	0·266	C_9 (CH)	0·071	0·475	C_{17} (CH)	0·005	0·446
C_2 (CH)	0·225	0·338	C_{10} (C)	0·872	0·734	C_{18} (CH)	0·929	0·525
Methyl cyanide								
C_{19} (CH_3)	0	0	C_{22} (C)	0	0	N_1 (N)	0	0
C_{20} (CH_3)	1/3	2/3	C_{23} (C)	1/3	2/3	N_2 (N)	1/3	2/3
C_{21} (CH_3)	2/3	1/3	C_{24} (C)	2/3	1/3	N_3 (N)	2/3	1/3

projected molecular length of 3·71 Å. From the latter and an assumed actual molecular length of 5·5 Å (as observed in other members of the series) the tilt θ of the molecule from the plane of the projection is calculated as 47½°. The vertical height from oxygen to oxygen is therefore 4·06 Å, 0·11 Å less than the distance between the centres of the hydrogen-bond hexagons, $2c/3$. This suggests that the hexagons are puckered so that the oxygen atoms are displaced alternately up and down from the mean plane by about 0·05 Å. In order to retain planar hexagons it is necessary to assume an error of 0·12 Å in the projected molecular length. The hydrogen bonds would then have a length of 2·84 Å. This alternative, though not ruled out, seems less probable.

The calculation of the 000*l* structure factors which might distinguish between the alternative structures is complicated by their dependence on the orientations of the three methyl cyanide molecules in the cell. These are known to be aligned (at least statistically) along the *c* axis, and their rotation about an axis perpendicular to *c* is greatly hindered.[3]

[2] Palin and Powell, *J.*, 1948, 571.
[3] Dryden, *Trans. Faraday Soc.*, 1953, **49**, 1333.

It might be expected that in a succession of cavities along the *c* axis there would be a tendency for the mutual action of dipoles to align the molecules head to tail. The pyroelectric effect observed is weak and this may arise through disorder in such a column of methyl cyanide molecules, through different orientations of whole columns, or through both effects. Some diffuse reflections observed on higher layer lines but not on the zero layer line of *c* axis oscillation photographs indicate that there is disorder. The rather low heights of the Fourier peaks corresponding to methyl cyanide can be explained, as in the case of the methanol compound,[2] by the movement, with restriction, of the molecules in their cavities.

The 000*l* structure factors were calculated for a number of different structural arrangements, which involved different degrees of puckering of the hydrogen-bond hexagons and different orientations of the methyl cyanide molecules in the cell. None of the arrangements tried gave completely satisfactory agreement with the observed F_{000l} but those with puckered hydrogen-bond hexagons were more favourable than those with planar hexagons. The best agreement was obtained with puckered hexagons and with one methyl cyanide molecule in the cell pointing in the opposite direction from the other two.

With a structure of this complexity and crystals subject to decomposition and disorder, it is unlikely that the precise nature of the minor distortions of the hydrogen-bond hexagons and the departure of the quinol molecules from the ideal positions can be established without an investigation disproportionate to its importance. It seems probable that both modes of distortion, extension and puckering of the hydrogen bond hexagons, occur, the latter effect being more prominent. These distortions account for the comparative instability of this member of the series of β-quinol clathrate compounds.

CHEMICAL CRYSTALLOGRAPHY LABORATORY,
UNIVERSITY MUSEUM, OXFORD.
[Present address (S. C. W.): DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, NOTTINGHAM.]

[*Received, April 18th,* 1956.]

---

949. *Aromatic Reactivity. Part I. Effects of Substituents on the Acid Cleavage of Phenyltrimethylsilanes*

By C. EABORN.

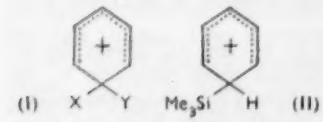
The acid-catalysed cleavage of some substituted phenyltrimethylsilanes in aqueous-methanolic perchloric acid has been studied spectrophotometrically for a range of activating and weakly deactivating substituents. The results provide a detailed picture of the effects of these substituents on electrophilic aromatic reactivity.

THE acid-catalysed solvolytic cleavage of aryl–Si bonds is an electrophilic aromatic substitution in which a proton, initially solvated, is the attacking species.[1] Since removal of a trimethylsilyl group from a benzene ring shifts the ultraviolet absorption spectrum about 3—15 mμ away from the visible region, with little change of shape, the reaction is easily followed spectrophotometrically and may be conveniently used to study the effects of nuclear substituents on aromatic reactivity. The results are free from uncertainties about the position of electrophilic attack which complicate the aromatic substitution processes normally studied.

It is generally accepted that electrophilic aromatic substitutions probably proceed through intermediates (σ-complexes) of type (I) (*e.g.*, in *tert.*-butylation, X = Bu^t, and

[1] (*a*) Eaborn, *J.*, 1953, 3148; (*b*) Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1954, **76**, 6353; (*c*) see also Baines and Eaborn, *J.*, 1956, 1436.

Y = H; in nitration, X = NO_2, Y = H),[2] and it is usually considered that in nitration and halogenation the formation of the intermediate is rate-determining,[2,3] but the kinetic isotope-effects on which these beliefs are based are not, in fact, conclusive.[4] The same uncertainty, namely, whether formation or destruction of the intermediate (II) is rate-determining, exists also in protodesilylation;* but this does not reduce the significance of effects of substituents since in all simple electrophilic aromatic substitutions the transition states for formation and destruction of the intermediate are likely to be close in structure to the intermediate and to one another, and effects of substituents will be much the same on both transition states and intermediate.[4]



(I) (II)

Table 1 lists first-order rate-constants for removal of the trimethylsilyl group in aqueous-methanolic perchloric acid, and the reactivities of monosubstituted phenyltrimethylsilanes relative to that of phenyltrimethylsilane. We draw attention to some particular features.

TABLE 1. *Cleavage of substituted phenyltrimethylsilanes by aqueous-methanolic* [a] *perchloric acid at* 51·2°

Subst.	$[HClO_4]$ (M) [b]	10^3k_1 (min.$^{-1}$)	Relative rate ($k_{rel.}$)	log $k_{rel.}$
p-NMe_2	0·001056	46	—	—
	0·01056	105		
	0·1056	116	*ca.* $3·0 \times 10^7$	7·5
	0·823	105		
	9·22	53·5		
2 : 4 : 6-Me_3	0·1056	24·2		
	0·440	116	53,600	4·73
	0·823	258		
p-OH	0·1056	4·91		
	0·440	23·5	10,700	4·03
	0·823	51·2		
p-OMe	0·823	7·19	1510	3·18
	2·35	39·8		
p-$Me_3Si{\cdot}CH_2$	2·35	8·3	315	2·50
	4·53	40·5		
o-OMe	4·53	43	335	2·53
p-Me	4·53	2·72	21·1	1·32(5)
	9·22	38		
p-Et	9·22	35	19·5	1·29
o-Me	9·22	32	17·8	1·25
p-Pr^i	9·22	31	17·2	1·24
p-Bu^t	9·22	28	15·6	1·19
m-$Me_3Si{\cdot}CH_2$	9·22	11·1	6·2	0·79
p-Ph	9·22	6·4	3·55	0·55
p-Me_3Si	9·22	4·5	2·5	0·40
m-Me	9·22	4·1	2·3	0·36
H	9·22	1·80	1	0·0
p-F	9·22	1·35	0·75	−0·12
p-Cl	9·22	0·24	0·13	−0·87
p-Br	9·22	0·18	0·10	−1·0

[a] See Experimental section. [b] Concn. of acid, 2 vol. of which were added to 5 vol. of methanol.

(a) *Alkyl substituents.* The activating effect of an *o*-Me group ($k_{rel.}$ 18) is close to that of the *p*-Me group ($k_{rel.}$ 21). This is in line with the closeness of the reactivity of *ortho*- and *para*-positions of toluene in reaction with the Br^+ or $HOBr^+$ ion (partial rate factors, 76 and 59, respectively [5]), and in tritiation in which the *ortho*- and *para*-positions are equally reactive within experimental error.[6] In nitration (partial rate factors, 42 and 58) and molecular halogenation (partial rate factors, 450 and 1990) steric hindrance is said to reduce the reactivity of the *ortho*-position.[5]

The suggestion has been made that *para*-alkyl groups will activate according to the hyperconjugative order (Me > Et > Pr^i > Bu^t) when the attack on the ring is by uncharged electrophilic reagents but according to the reverse, inductive order when attack is by a positive entity.[7] However, in protodesilylation,* in which attack is by a positive

* Removal of a trimethylsilyl group would be described as "detrimethylsilylation" in a suggested systematic nomenclature (*J.*, 1954, 4717), but the less formidable "desilylation" will be used in this series to denote removal of a silicon atom along with the attached groups. The replacing group will normally be specified, as in "bromodesilylation," but "protodesilylation" will often be shortened to "desilylation" when no confusion can arise.

[2] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, Ltd., London, 1953, Chap. VI.
[3] Melander, *Arkiv Kemi*, 1950, **2**, 211; Berglund-Larrson and Melander, *ibid.*, 1953, **6**, 219.
[4] Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.
[5] de la Mare and Harvey, *J.*, 1956, **36**.
[6] Olsson and Melander, *Acta Chem. Scand.*, 1954, **8**, 523.
[7] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

entity, the hyperconjugative order is followed, just as it is in molecular halogenation (and also in molecular bromodesilylation). The sole example of the *p*-Bu[t] group's activating more than the *p*-Me group in an electrophilic aromatic substitution is in nitration.[8]

(b) *Organosilyl substituents.* Because of the opposition of $+I$ and $-T$ effects the trimethylsilyl group supplies electrons to the ring or withdraws them according to the demand.[9] Nitration studies have shown the group to be slightly activating and weakly *ortho-para*-directing.[10] Our results show it to activate slightly more from the *para*-position than does the methyl group from the *meta*-position.

The trimethylsilylmethyl group is strongly electron-supplying,[11] and the strong activation of the *para*-positions was expected. We believe that the large difference in activating power of this group in the *para*- and the *meta*-position (the activation ratio is 60 : 1 compared with 10 : 1 for the methyl group) arises from hyperconjugation of the type (A), since this could operate directly only to *ortho*- and *para*-positions.[11] Even so, activation by the *m*-$Me_3Si{\cdot}CH_2$ group is anomalously low in view of its quite large inductive effect,[11] and it is possible that steric hindrance to solvation is important since this bulky group must interfere with solvent approach to both positions *ortho* to itself, on which a substantial portion of the positive charge resides in the transition state.

(c) *Methoxy- and hydroxy-substituents.* The *p*-OH group activates several times more strongly than the *p*-OMe group. This cannot arise from the formation from the phenol of small amount of the highly reactive phenoxide ion, *p*-$Me_3Si{\cdot}C_6H_4{\cdot}O^-$, since this would be suppressed by increasing the concentration of acid, whereas the rate of reaction of the

(A) (B)

phenolic compound shows the same dependence on concentration of acid as that of other compounds (*e.g.*, the ratios of the rate constants for 2-mesityl- and *p*-hydroxyphenyltrimethylsilane are 5·0, 4·95, and 4·93 for acid concentrations *ca.* 0·8, 0·4, and 0·1M respectively). de la Mare and Robertson have suggested that the activating power of the *p*-OH group is greater than that of the *p*-OMe group because of the hyperconjugation shown in (B), but at least equally important could be hydrogen bonding between the solvent and the hydroxyl group (*i.e.*, $\begin{matrix}Me\\H\end{matrix}\!\!>\!O\cdots H{-}O{-}C_6H_4{\cdot}SiMe_3$) which increases the electron-release of the latter. (The hydrogen bonding and hyperconjugation would, in fact, interact to reinforce each other.)

The relative activating effects of *p*-OMe and *o*-OMe groups (4·5 : 1), which reflect the stronger operation of the $-I$ effect from the *ortho*-position, agree with those in replacement of deuterium by protium in which *p*-deuteroanisole is 3 times as reactive as *o*-deuteroanisole at 80°.[12]

(d) p-*Dimethylamino-substituent.* The very great activating power of this group is clearly shown in Table 1, and our results confirm the rather indirect deductions from molecular halogenation.[13] The value of $k_{rel.}$ is arrived at in the following way.

p-Dimethylaminophenyltrimethylsilane reacts at an 0·01056M(added)-acid concentration some 4·3 times as fast as mesityltrimethylsilane with 0·1056M-acid, and thus approximately 43 times as fast as the mesityl compound would react in the weaker acid

[8] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.
[9] Benkeser and Krysiak, *J. Amer. Chem. Soc.*, 1953, **75**, 2421; Eaborn and Parker, *J.*, 1955, 126; Chatt and Williams, *J.*, 1956, 688.
[10] Speier, *J. Amer. Chem. Soc.*, 1953, **75**, 2930.
[11] Eaborn and Parker, *J.*, 1954, 939.
[12] Lauer and Day, *J. Amer. Chem. Soc.*, 1955, **77**, 1904.
[13] de la Mare, *J.*, 1954, 4450.

(actually rather more, since the rate falls off rather more rapidly than the acid concentration). In the reaction medium, with 0·01056M(added)-acid, 9·6% of *NN*-dimethylaniline is found spectrophotometrically to be present as free amine, and since the *p*-trimethylsilyl derivative is a slightly weaker base rather less than 9·6% of it will be present as the free amine. Thus *p*-dimethylaminophenyltrimethylsilane is at least 430 times as reactive as the mesityl compound, and $>2{\cdot}3 \times 10^7$ times as reactive as phenyltrimethylsilane. A similar figure can be deduced from the rate in $0{\cdot}1056 \times 10^{-2}$M(added)-acid, when 48% of *NN*-dimethylaniline is present as free base. We believe the figure of $3{\cdot}0 \times 10^7$ in Table 1 to be accurate within 25%.

p-Dimethylaminophenyltrimethylsilane reacts at a maximum rate with *ca.* 0·1M(added)-acid. At greater concentrations the rate falls slowly, the rates at 0·83M- and 9·2M-acid being 0·90 and 0·46 of that at 0·1056M-acid concentration, whereas rate increases of *ca.* 10 and 370 respectively would be found for other compounds. This behaviour is to be expected from our previous observation that the rate of desilylation is proportional to the proton-donating power of the medium as measured by the indicator ratio, $[BH^+]/[B]$, for a neutral base, B, (*p*-nitroaniline being the base employed).[13a] Since with acid concentration at least 0·1M(added) the *p*-dimethylaminophenyltrimethylsilane is almost all in the protonated form (which reacts at a negligible rate), the concentration of the latter changes inappreciably, and increasing the acid strength to double the indicator ratio for this base doubles the rate at which the free amine reacts but halves its concentration. The apparent rate would thus be independent of the acid concentration if it were not that (*a*) the variation of rate with the indicator ratio, $[BH^+]/[B]$, is not completely independent of the base, B,[13c] and (*b*) at a given indicator ratio for a particular base the rate of desilylation falls as the proportion of water in the medium decreases.[13a] Since our method of making up the reaction mixture means that less water is present in the more strongly acidic media, a slight fall in the rate of reaction of *p*-dimethylaminophenyltrimethylsilane will result from an increase in the concentration of added acid.

Below *ca.* 0·1M(added)-acid the change in concentration of protonated base can no longer be neglected, and the apparent rate of reaction will begin to fall markedly as the concentration of acid is lowered, since the indicator ratio, $[BH^+]/[B]$ (and thus the rate of reaction of the free amine), falls more rapidly than the concentration of free amine increases.

Correlation with Other Electrophilic Reactions.—With the figures available in Table 1 it is possible to test proposals that a free energy relation of the Hammett type, $\log k_{rel.} = \rho\sigma^+$, may apply to electrophilic aromatic substitutions or to reactions forming carbonium ions adjacent to the ring, σ^+ being characteristic of the substituent for these reactions, and ρ characteristic of the reaction.[14] If the proposals are valid, then $\log k'_{rel.}/\log k_{rel.}$ should be constant for the various substituents where $\log k_{rel.}$ refers to desilylation and $\log k'_{rel.}$ refers to some other electrophilic reaction. Table 2 gives some values of this ratio for an aromatic substitution involving a molecular reagent and one involving a positive ion, for the migration step of the pinacol rearrangement (which may be looked upon as an electrophilic aromatic substitution in which attack of a carbonium ion breaks a C–C bond), and for two S_N1 solvolysis reactions involving production of carbonium ions adjacent to the ring.

The striking features of this Table are: (*a*) the reasonable constancy of the $\log k'_{rel.}/\log k_{rel.}$ ratios for substituents *m*-Me, *p*-Me, *p*-OMe, *p*-OH, and *p*-MNe_2; and (*b*) the considerable deviations in most cases of the ratios for *p*-Ph and *p*-halogen substituents, the deviations being such that desilylation is several times slower than might have been expected. The strong deactivating effect of a *p*-Cl substituent is not an abnormality to be attributed to some special features of this reaction, since similar deactivation is found in nitration, and it is significant that this is the reaction which most closely resembles desilylation, both being displacements at a ring-carbon atom by a positive reagent. (The deactivating effects of a *p*-F substituent are also similar

[14] (*a*) Pearson, Baxter, and Martin, *J. Org. Chem.*, 1952, **17**, 1511; (*b*) Kochi and Hammond, *J. Amer. Chem. Soc.*, 1953, **74**, 3445; (*c*) Tsurata, *Bull. Inst. Res. Kyoto Univ.*, 1954, **32**, 149; (*d*) McGary Okamoto, and Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 3037; (*e*) Miller, *Austral. J. Chem.*, 1956, **9**, 61.

bond. Phenyltrimethylsilanes are stabilized by d_π–p_π bonding, and this will be most

in the two reactions, whereas a *p*-F substituent activates in molecular halogenation and in brominolysis of benzeneboronic acids,[15] and facilitates the ionization of triphenylmethyl chloride.[16]) It thus appears that while a satisfactory set of σ^+-constants may well be found for some of the substituents listed in Table 1, the influence of some others, such as *p*-Cl and *p*-Ph, will vary too greatly with the electrical demands to be expressed adequately by single σ^+ constants. It is not surprising that the *p*-Ph group should behave abnormally, since this substituent is so sensitive to electron-demand that it is one of only two groups known clearly to activate in both electrophilic and nucleophilic aromatic substitutions.[14b]

TABLE 2. *Substituent effects in desilylation and other electrophilic reactions : values of* $\log k'_{rel.}/\log k_{rel.}$

	Mol. halogn.[a]	Pinacol rearr.[b]	Hydrolysis of $R{\cdot}C_6H_4{\cdot}CH_2{\cdot}O{\cdot}Tos$ [c]	Ethanolysis of $(R{\cdot}C_6H_4)_2CHCl$ [d]	Nitration [e]
p-NMe_2	2·6	—	—	—	—
p-OH	2·9	—	—	—	—
p-OMe	3·1	0·85	1·36	0·97	—
p-Me	2·5	0·96	1·12	0·92	1·3
p-Alkyl	2·4 [f]	0·78 [g]	—	1·02 [h]	—
m-Me	—	0·78	0·7	0·89	1·1
p-Ph	0·0	1·90	—	1·91	—
p-F	— [i]	—	—	—	0·93
p-Cl	0·46	0·18	—	0·48	1·0
p-Br	0·6	—	0·4	0·33	1·0

[a] Halogenation of $R{\cdot}C_6H_5$ in acetic acid.[13] [b] $k'_{rel.}$ is the migratory aptitude of $R{\cdot}C_6H_4$ relative to C_6H_5 in rearrangements of $[(R{\cdot}C_6H_4)(C_6H_5)C(OH)]_2$ (Bachmann and Ferguson, *J. Amer. Chem. Soc.*, 1934, **56**, 2081). [c] S_N1 hydrolysis of benzyl toluene-*p*-sulphonates in aqueous acetone.[14b] [d] S_N1 reaction (Norris and Banta, *J. Amer. Chem. Soc.*, 1928, **50**, 1804). [e] Ref. 2, p. 247; $\log k'_{rel.}$ for *p*-F (− 0·11) is obtained from the rate data on p. 246, and the orientation data on p. 260 of ref. 2. [f] R = Bu^t. [g] R = Pr^i. [h] R = Et. [i] $\log k'_{rel.} = 0·8$; $\log k_{rel.} = -0·11$.

A set of σ^+ constants has recently been proposed by Miller,[14e] but since these are based exclusively on results for molecular halogenation, to test them against our data would yield no information not indicated by the first column of $\log k'_{rel.}/\log k_{rel.}$ ratios in Table 2. A similar argument applies to σ^+ constants derived from solvolysis of benzyl toluene-*p*-sulphonates.[14b] It has recently been suggested that for *meta*-substituents $\sigma^+ = \sigma$ (where σ is the usual Hammett σ constant for nucleophilic side chain reactions [17]), while for *para*-substituents [14d] $\sigma^+ = \sigma - 0·134$. A set of σ^+ constants so derived does not stand up to the test of our data, a plot of $\log k_{rel.}$ against σ^+ showing continuous curvature, as indicated by the following values of $\log k_{rel.}/\sigma^+$:

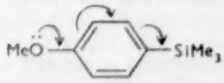
R	*p*-NMe_2	*p*-OH	*p*-OMe	*p*-$Me_3Si{\cdot}CH_2$	*p*-Me	*p*-Ph	*m*-Me	*p*-Cl	*p*-Br
$-\sigma$	0·600	0·357	0·268	0·260 [11]	0·170	−0·009	0·069	−0·227	−0·232
$-\sigma^+$	0·734	0·491	0·402	0·394	0·304	0·125	0·069	−0·093	−0·098
$-\log k_{rel.}/\sigma^+$ ...	10·3	8·2	7·9	6·3	4·3	4·4	5·2	9·4	10·2

However, we understand from Professor H. C. Brown that he has devised a new set of σ^+ constants based upon the rates of solvolysis of substituted $\alpha\alpha$-dimethylbenzyl halides and that these can be correlated with the data of Table 1 and with those for fifteen other electrophilic reactions at least as well as σ constants are correlated with nucleophilic side-chain reactions. We believe, nevertheless, that with this, and all, sets of σ^+ constants there will inevitably be serious deviations from correlation in the case of certain substituents such as *p*-halogeno and *p*-phenyl, as indicated by the data of Table 2, particularly in substitutions at a ring-carbon atom as distinct from reactions involving electrophilic attack in a side-chain.

Special Features of Desilylation.—Comparisons of effects of substituents in this reaction with those in halogenation and nitration reveal no special features arising from the fact that in the former reaction a C–Si bond is being broken instead of a C–H

[15] Kuivala and Benjamin, *J. Amer. Chem. Soc.*, 1955, **77**, 4834.
[16] Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 470.
[17] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

bond. Phenyltrimethylsilanes are stabilized by $d\pi$–$p\pi$ bonding, and this will be most marked when substituents with $+T$ effects are present in the *para*-position [cf. the effects shown in (C)], but since such a substituent will probably stabilize phenyltrimethylsilane in proportion as it stabilizes benzene the effects of substituents relative to one another will not differ much in removal of trimethylsilyl and in the more familiar aromatic substitutions.

(C) 

The fact that a C–Si bond is being broken and not a C–H bond seems to decrease the spread of reactivities of substituted compounds (or the slope, ρ, of a plot of log $k_{rel.}$ against σ^+). Thus Melander [6] has shown that in acid-catalysed isotopic exchange, which is also an aromatic substitution by a positive hydrogen ion, the *para*-position of toluene is activated some 32 times as strongly as the *meta*, whereas a ratio of 9 applies in desilylation. This is expected, since the more electropositive the group being removed from the ring the greater will be the fraction of positive charge residing on it in the transition state, and the smaller that on the ring, so that the electrical effects of substituents will have smaller influence.

Experimental

M. p.s and b. p.s are corrected.

Materials.—The compounds employed have been previously described, except p-tert.-*butylphenyltrimethylsilane*, m. p. 78° (from aqueous ethanol) (Found: C, 75·6; H, 10·8. $C_{13}H_{22}Si$ requires C, 75·7; H, 10·4%), and p-iso*propylphenyltrimethylsilane*, b. p. 126—127°/40 mm., 222°/750 mm., n_D^{20} 1·4914 (Found: C, 75·0; H, 10·5. $C_{12}H_{20}Si$ requires C, 74·9; H, 10·5%) which were prepared from trimethylchlorosilane and the appropriate arylmagnesium bromide in ether. In all preparations from aryl bromides care was taken to ensure that no bromide remained unchanged before coupling with the silicon halide, as the bromides boil close to the corresponding trimethylsilyl compounds.

The following physical constants for $R{\cdot}C_6H_4{\cdot}SiMe_3$ compounds are new or are believed to be superior to those in the literature: R = *p*-Cl, b. p. 211·5°, m. p. 0·0°, n_D^{20} 1·5097; *p*-Ph, m. p. 55·5° (from ethanol); *p*-OH, m. p. 76° (from light petroleum); *p*-NMe_2, m. p. 27·5°; *p*-$Me_3Si{\cdot}CH_2$, m. p. 16·5°.

p-Bromophenyltrimethylsilane, b. p. 230°, n_D^{20} 1·5284 (prepared from *p*-bromophenylmagnesium bromide and trimethylchlorosilane), probably contained small quantities of *p*-dibromobenzene and *p*-di(trimethylsilyl)benzene which are very difficult to remove. The former does not interfere in the rate studies (other than by altering the absolute values of the optical density), while the effect of the latter was minimized by neglecting the first 24 hr. of reaction, during which most of the di(trimethylsilyl)benzene is converted into benzene.

Apparatus.—For most of the rate studies a thermostatically controlled cell-holder was used in the Unicam S.P. 500 spectrophotometer. This holder (designed by Dr. N. Macleod) fitted on to the usual movable cell-carrier, and consisted of a block of copper with drilled spaces for two stoppered 1 cm. quartz cells and for the light beam. A heating coil in the block was controlled by a Mullard Temperature Controller Type E7594 actuated by a thermistor in contact with the base of the block between the cells. The absorption cells fitted closely to the metal, so that aqueous methanol in a cell at *ca.* 18° placed in the block reached the temperature of the block (51·2°) in less than 4 min. The subsequent temperature variation could not be detected on a sensitive Anschütz thermometer placed in the liquid, either during a heating–cooling cycle or in the course of a day, and was certainly $<0·02°$.

Rate Measurements.—The ultraviolet absorptions of solutions of the organosilicon compound, $R{\cdot}C_6H_4{\cdot}SiMe_3$, and the parent compound, $R{\cdot}C_6H_5$, were examined in methanol, and wavelengths selected for following the removal of trimethylsilyl. Usually two or more wavelengths were employed, and in all reported cases rate constants measured at different wavelengths did not differ by more than 2%. Although rate constants were reproducible to within $\pm 1\%$ and excellent first-order constants were obtained throughout the course of a reaction, often up to 90% completion, the accuracy of spectrometric methods is greatly influenced by impurities, and we believe that the absolute values of the rate constants quoted in Table 1 may be in error by as much as $\pm 3\%$ for liquid aryltrimethylsilanes (possibly $\pm 6\%$ for the *p*-bromo-compound) but by rather less for solids, which could be obtained pure with certaintly. The ratio of the

rate constants for one compound at two acid concentrations, sometimes used in the "overlap" procedure for calculating values of $k_{rel.}$ in Table 1, is more accurate.

For reactions which could be completed in a day, 10 ml. of aqueous acid were added to 25 ml. of a solution of the organosilane in redistilled "AnalaR" methanol, and some of the mixture was transferred to a 1 cm. stoppered quartz cell which was then placed in the cell-block thermostat described above. Absorption readings (relative to methanol) were begun after not less than 8 min. Reactions were taken to completion (*i.e.*, to 10 half-lives) in the cell when the half-life was $\lesssim \frac{1}{2}$ hr., but in other cases "infinity" values were obtained from samples of the reaction mixture kept in sealed tubes at 51° for a period equivalent to 10 half-lives, or at 70° for a period equivalent to 1—1·5 half-lives.

For slower reactions (R = *p*-Br, *p*-Cl, *p*-F, H, *m*-Me) 20 ml. of aqueous acid and 50 ml. of methanolic silane derivative were mixed, and samples (*ca.* 3 ml.) were sealed in drawn-out test-tubes which were then placed in a thermostat at 51·2°. "Zero time" readings were taken on samples withdrawn after *ca.* 30 min., quickly cooled to room temperature, and examined in 5 mm. cells.

The first-order rate constants, k_1, are given by the equation, $k_1 t = \ln[(D_0 - D_\infty)/(D_t - D_\infty)]$, where D_t is the optical density at time t, D_0 that at zero-time, and D_∞ that at infinity.

Table 3 shows the wavelengths at which measurements were made and the concentrations of the methanolic solutions of the silanes, $R{\cdot}C_6H_5{\cdot}SiMe_3$, these usually being such that optical density readings were between 0·9 and 0·05.

TABLE 3.

R	Concn. (M)	λ (mμ)	R	Concn. (M)	λ (mμ)
p-OH	15×10^{-4}	241, 283 [a]	*p*-Pr^i	25×10^{-4}	233·6
,,	,,	241, 284 [b]	*p*-Bu^t	4×10^{-4}	234
,,	,,	240·4, 283 [c]	,,	8×10^{-3}	266
p-NMe$_2$	6×10^{-3}	270 [a, c, d]	*o*-Me	1×10^{-3}	278
,,	7×10^{-4}	268, 274 [c]	,,	1×10^{-4}	230
,,	6×10^{-5}	266 [f]	*m*-Me	12×10^{-3}	270, 277
p-OMe	1×10^{-3}	282	H	14×10^{-3}	264, 231
p-Ph	6×10^{-5}	264, 272	*p*-Me$_3$Si	4×10^{-3}	278 [g]
p-Me$_3$Si·CH$_2$	75×10^{-4}	280	*o*-OMe	2×10^{-4}	228
,,	15×10^{-4}	248	,,	12×10^{-4}	287
m-Me$_3$Si·CH$_2$	3×10^{-3}	283, 275	*p*-F	1×10^{-1}	271·5, 225
p-Me	1×10^{-3}	273	*p*-Cl	1×10^{-2}	238, 239
p-Et	7×10^{-5}	235·4	*p*-Br	1×10^{-2}	275, 250
p-Pr^i	5×10^{-5}	271			

[a] $[HClO_4] = 0{\cdot}1$M. [b] $[HClO_4] = 0{\cdot}4$M. [c] $[HClO_4] = 0{\cdot}8$M. [d] $[HClO_4] = 9{\cdot}2$M. [e] $[HClO_4] = 0{\cdot}01$M. [f] $[HClO_4] = 0{\cdot}001$M. [g] Phenyltrimethylsilane and benzene have low and similar absorptions at this wavelength, so that the change in absorption reflects the disappearance of *p*-trimethylsilylphenyltrimethylsilane.

NN-Dimethylaniline in Acidic Aqueous Methanol.—The optical densities, O.D., at 51·2°, of mixtures of 25 ml. methanolic solution of the base, or its methochloride with 10 ml. of aqueous acid (of concn. shown) were determined in 1 cm. stoppered cells at 249 mμ (a maximum for the free base):

Compound	Concn. (M)	$[HClO_4]$ (M)	O.D.	$Ph{\cdot}NMe_2$ (%)
$Ph{\cdot}NMe_2$	7×10^{-5}	0	0·545	100
$Ph{\cdot}NMe_2$	7×10^{-4}	$1{\cdot}506 \times 10^{-2}$	0·543	9·6
$Ph{\cdot}NMe_2{\cdot}Cl^-$	7×10^{-4}	$1{\cdot}506 \times 10^{-2}$	0·024	0
$Ph{\cdot}NMe_2$	7×10^{-5}	$1{\cdot}506 \times 10^{-3}$	0·259	48
$Ph{\cdot}NMe_2{\cdot}Cl^-$	7×10^{-5}	$1{\cdot}506 \times 10^{-3}$	0·000	0

Some of the compounds used were made by Mr. J. B. Hurd, who also carried out some preliminary reactivity studies.

UNIVERSITY COLLEGE, LEICESTER. [*Received, July 2nd,* 1956.]

950. *Phosphorescence and Fluorescence of Some Aromatic Nitro-amines.*

By R. Foster, D. Ll. Hammick, G. M. Hood, and A. C. E. Sanders.

Hitherto undetermined phosphorescence bands of a number of aromatic nitro-amines have been measured in the region 400—800 mμ. The effects of methyl and ethyl groups as substituents on the phosphorescence and fluorescence have been noted and discussed particularly in the light of their possible steric effects.

The phenomenon of phosphorescence of organic compounds in rigid media was observed as early as 1896 by Schmidt,[1] but it is only recently that a satisfactory explanation of it has been given. Molecules in their ground state (N) on absorption of light of sufficient energy, exist for a short time, about 10^{-9} sec., in the first excited state (F) from which they normally return to the ground state either by a radiationless, thermal process or by the emission of light, *i.e.*, fluorescence. Jablonski [2] postulated the existence of another, metastable, state (P) of lower energy than the state F and suggested that instead of going directly to the ground state some of the molecules in the state F might pass into a P state. Phosphorescence is the emission of radiation when molecules return to the ground state from this P state. Lewis and Kasha [3] produced experimental evidence that the P state is the first triplet level of a molecule whose ground state is a singlet. This has been confirmed by direct observation of paramagnetism in molecules which have been excited to this state [4] and also during phosphorescence.[5] The fact that the transitions between triplet and singlet levels are formally forbidden results in the relatively long period required for the complete emission of such radiation, which is the characteristic of phosphorescence. If the substance is held in a rigid medium at a low temperature, the likelihood of the energy of the P state being lost by thermal collisions, rather than by phosphorescence emission, is reduced.

p-Nitroaniline has been reported by Lewis and Kasha [3] to show strong phosphorescence when cooled in a rigid medium to −180°. We have now investigated the phosphorescence and incidentally the fluorescence of a number of methyl- and ethyl-substituted *p*-nitroanilines under such conditions.

Experimental

We are indebted to Dr. E. J. Bowen, F.R.S., for the loan of apparatus for the examination of phosphorescence and fluorescence spectra.[6] The light source is supplied by an alternating current of 50 cycles/sec. The amplifier responds only to multiples of 50 cycles/sec. Because of the short lifetime of the fluorescent state, any fluorescence emission of the material under examination will alternate in intensity with the same frequency as the intensity of the incident light which, being supplied with 50 cycles/sec. A.C., will alternate 100 times a second. Thus the light from the spectrometer will cause a varying current in the photomultiplier tube, and because its frequency will be a multiple of 50 cycles/sec., the signal will be accepted by the amplifier. The same will be true of phosphorescence provided that its lifetime is shorter than, or of the same order as, the time of alternation of the light source. But with phosphorescence of longer lifetime, *viz.*, 10^{-1} sec. or longer, the current produced in the photomultiplier tube will be steady and will be rejected by the amplifier. Consequently, when the spectrum is scanned, only fluorescence and short-lifetime phosphorescence is measured. We have modified the system by inserting a rotating shutter in the path of the light just before it enters the spectrometer, arranged so that the light emitted from the material under examination is chopped at a rate which is a multiple of 50 cycles/sec. (actually a shutter of 4 sectors rotating at 1500 r.p.m. is used) so that the sum of the fluorescence and phosphorescence emissions is measured because

[1] Schmidt, *Ann. Physik*, 1896, **58**, 103.
[2] Jablonski, *Nature*, 1933, **131**, 839; *Z. Physik*, 1935, **94**, 38.
[3] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1944, **66**, 2100.
[4] Lewis, Calvin, and Kasha, *J. Chem. Phys.*, 1949, **17**, 804.
[5] Evans, *Nature*, 1955, **176**, 777.
[6] Bowen and Brocklehurst, *J.*, 1954, 3875.

all the emitted light is varying in intensity with a frequency which is a multiple of 50 cycles/sec. By scaling up the intensities obtained in the determination in which the rotating shutter is used, to compensate for the masking effect of the shutter, and subtracting the resultant curve from that obtained in a determination in which no shutter is used, a phosphorescence spectrum is obtained (provided its lifetime is greater than 10^{-1} sec.).

Solutions.—The solvent used in all the measurements of emission spectra was a mixture of ethanol and methanol (5 : 1 v/v). The alcohols were purified by fractionation through a 40 cm. column of glass helices. The concentrations of all the solutions were 10^{-2}—10^{-3}M.

Accuracy.—In the spectra, some of the bands, particularly the fluorescence bands, flatten near the maximum, there presumably being unresolved vibration structure in the bands. The maximum recorded is the intersection of the line joining the mid-points of the tie lines with the envelope of the absorption curve. In successive determinations a reproducibility of ± 50 cm.$^{-1}$ was obtained in the case of the fluorescence spectra, and ± 25 cm.$^{-1}$ in that of the phosphorescence spectra.

Preparation of Materials.—Most of the compounds were prepared by standard procedures and recrystallised to constant m. p. In particular, 2 : 6-dimethyl-4-nitroaniline was prepared by Wepster's method.[7] *N* : *N* : 2 : 6-*Tetramethyl-4-nitroaniline* appears not to have been made before. It was prepared by heating 2 : 6-dimethyl-4-nitroaniline (4 g.) and methyl iodide (5 ml.) with methanol (12 ml.) in a sealed tube at 130° for 12 hr. The product was extracted with acid, precipitated by addition of ammonia solution, and recrystallised from aqueous ethanol (1 : 1 v/v). The colour was removed by elution from activated alumina by light petroleum (b. p. 60—80°); m. p. 68° (yield 30%) (Found: C, 62·2; H, 7·2; N, 14·2. $C_{10}H_{14}O_2N_2$ requires C, 61·8; H, 7·2; N, 14·4%).

	Emission		Absorption [a]	
	ν (phos.) (cm.$^{-1}$)	ν (fluor.) (cm.$^{-1}$)	ν (cm.$^{-1}$)	$\varepsilon \times 10^{-3}$
4-Nitroaniline	19,400 [b]	—	27,010 [c]	16·2 [c]
2-Methyl-4-nitroaniline	19,150	—	26,390 [d]	17·4 [d]
N-Methyl-4-nitroaniline	19,025	—	25,600 [c]	18·4 [c]
NN-Dimethyl-4-nitroaniline	18,975	21,450	25,600 [c]	19·0 [c]
2 : 6-Dimethyl-4-nitroaniline	18,950	—	26,700	14·2
N : 2-Dimethyl-4-nitroaniline	18,925	—	25,840	15·3
N : *N* : 2-Trimethyl-4-nitroaniline	18,800	20,950	27,100	10·1
N : *N* : 2 : 6-Tetramethyl-4-nitroaniline	18,650	19,625	26,800	5·6
3-Methyl-4-nitroaniline	—	—	27,030	12·8
3 : 5-Dimethyl-4-nitroaniline	—	—	25,890	5·0
2 : 3 : 5 : 6-Tetramethyl-4-nitroaniline	—	—	25,580	1·5
N-Ethyl-4-nitroaniline	19,025	—	—	—
NN-Diethyl-4-nitroaniline	18,875	20,775	—	—
3-Nitroaniline	—	19,100	—	—
6-Methyl-3-nitroaniline	—	19,150	—	—
2-Methyl-3-nitroaniline	—	19,025	—	—
NN-Dimethyl-3-nitroaniline	—	18,875	—	—
2-Nitroaniline	—	19,725	—	—
4-Methyl-2-nitroaniline	—	19,225	—	—
4-Nitro-1-naphthylamine	17,300	—	—	—
6-Nitro-2-naphthylamine	—	19,900	—	—
4-Amino-4′-nitrodiphenyl	—	19,150	—	—
4 : 4′-Dinitrodiphenyl	20,125 [f]	—	—	—

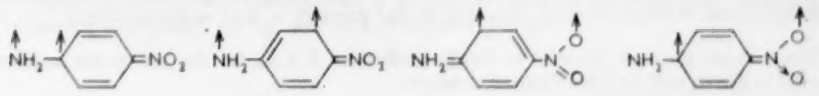
[a] In ethanol. [b] Lewis and Kasha [3] give 19,300 cm.$^{-1}$. [c] Glotz, *Bull. Soc. chim. France*, 1934, **1**, 1148. [d] Morton and McGookin, *J.*, 1934, 904. [e] Kumler, *J. Amer. Chem. Soc.*, 1946, **68**, 1185. [f] Lewis and Kasha [3] give 20,200 cm.$^{-1}$.

Discussion

In Lewis and Kasha's [3] triplet state a pair of electrons has become uncoupled and have parallel spins. We may attempt to deduce structures for such states. In *p*-nitroaniline it seems likely that the uncoupled electrons will be disposed in such a way that there is a general accession of negative charge to the nitro-group and away from the amino-group. Of the more obvious structures (I)—(IV) we select tentatively (IV) as complying with this requirement and also giving the best interpretation of our results. The stability of such a structure could be modified by substituents which alter the electron density within the benzene ring or which by steric interference with the nitro-group increase its energy by disturbing the planarity requirements for resonance of the nitro-group with the ring. The

[7] Wepster, *Rec. Trav. chim.*, 1954, **73**, 809.

steric interference of the methyl groups *ortho* to the nitro-group is apparently sufficient to disallow phosphorescence of longer than 10^{-1} sec. life; for example, 3-methyl-4-nitroaniline and 3 : 5-dimethyl-4-nitroaniline do not phosphoresce under our conditions. Other evidence of steric interference between these groups may be found in the relatively low extinction coefficients of certain absorption bands of these compounds (see col. 5 of Table). This conclusion is also reached by Remington [8] and is supported by the work of Stewart [9] who measured the heat of combustion of *o*-nitrotoluene and deduced that an energy of 7·6 kcal. would be required to force the methyl and nitro-groups into the plane of the benzene ring. Similar steric prevention of planarity of a dimethylamino-group with the benzene ring should result from *ortho*-methyl groups. Klevens and Platt [10] deduced that the dimethylamino-group in *N* : *N* : 2 : 6-tetramethylaniline is twisted 90° out of the plane



(I) (II) (III) (IV)

The symbol ↑ represents an uncoupled electron.

of the benzene ring. From the absorption spectra (see Table), the extinction coefficients of *N* : *N* : 2-trimethyl- and *N* : *N* : 2 : 6-tetramethyl-4-nitroaniline are small compared with the extinction coefficient of *NN*-dimethyl-4-nitroanilne itself, giving a further indication of the steric effect. From the Table it will be seen that substitution *ortho* to the amino-group does not inhibit phosphorescence; this is to be expected, because in structure (IV) the amino-group is not conjugated with the ring, and interference with its rotation does not affect the planar resonance structure.

Apart from the steric effects, the alkyl groups substituted in any position will modify the energy of the structure by their inductive effects. The magnitude of the inductive effect may be expected to vary with the position of the group. Our results, however, show little more than that the phosphorescence frequencies and hence energies fall as more alkyl groups are introduced. Thus the phosphorescence energies decrease in the series : *p*-nitroaniline, and 2-methyl-, *N*-methyl-, *NN*-dimethyl-, 2 : 6-dimethyl-, *N* : 2-dimethyl-, *N* : *N* : 2-trimethyl-, and *N* : *N* : 2 : 6-tetramethyl-4-nitroaniline.

No phosphorescence was observed with the *o*- or *m*-nitroanilines. In the case of *m*-nitroaniline no structure corresponding to (IV) can be drawn and in that of *o*-nitroaniline some *ortho*-effect may be operating. It is possible, of course, that the phosphorescence is too short-lived to be measured on our instrument, or alternatively, that there is 100% fluorescence so that the *P* state is not occupied.

4-Nitro-1-naphthylamine phosphoresces strongly. This compound may be regarded as 4-nitro-2 : 3-benzoaniline and it might be expected that the energy of the phosphorescent state would be lower than that of *p*-nitroaniline because of the increased conjugation. This agrees with the experimentally determined value (17,300 cm.$^{-1}$) compared with that of *p*-nitroaniline (19,400 cm.$^{-1}$), which is close to that obtained by Lewis and Kasha [3] for 5-nitro-1-naphthylamine (17,900 cm.$^{-1}$). It is difficult to see why neither 6-nitro-2-naphthylamine nor 4-amino-4′-nitrodiphenyl phosphoresces, though it may be that all the energy of excitation is lost as fluorescence. It is interesting that 4 : 4′-dinitrodiphenyl, which does not fluoresce, has a phosphorescence band at 20,125 cm.$^{-1}$, which is close to that obtained by Lewis and Kasha for nitrobenzene (21,100 cm.$^{-1}$).

Fluorescence.—In the *p*-nitroaniline series of compounds, only the *NN*-disubstituted compounds fluoresce. Lippert [11] has suggested that a decrease in the electron-repelling power of the amino-group in going from NMe_2 to NH_2 has the effect of increasing the frequency of the fluorescence emission band. He concludes that, for all the primary and

[8] Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838.
[9] Stewart, *Phys. Rev.*, 1931, **38**, 1372.
[10] Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714.
[11] Lippert, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 328.

secondary *p*-nitroanilines, the energy of excitation will be greater than the bond energy, so that dissociation of the carbon–nitrogen bond occurs; hence there is no fluorescence. For solutions in dimethylformamide, this dissociation would appear to occur at about 20,000 cm.$^{-1}$. In the mixed alcohol solvent used in the present work a rather higher limit would be indicated, as compounds with a fluorescence band at 21,450 cm.$^{-1}$ have been measured. An alternative explanation, which appears to be less satisfactory, is that the primary and secondary amines may associate by hydrogen bonding. It is known that hydrogen bonding can facilitate the degradation of electronic energy and so quench fluorescence. Furthermore, there is evidence that in the solid state there is hydrogen bonding in the case of *p*-nitroaniline,[12] and in polar solvents between an amino-nitrogen atom and the solvent.[13] Such effects are, of course, not possible with the tertiary amines. However, it is difficult to see how this explanation could be applied to the fluorescence of 6-nitro-2-naphthylamine, 4-amino-4′-nitrodiphenyl, or the primary *o*- and *m*-nitroanilines.

The authors are most grateful to Dr. E. J. Bowen, F.R.S., for the use of the apparatus referred to above, and for his helpful discussions.

Dyson Perrins Laboratory, Oxford University. [*Received, July 6th*, 1956.]

[12] Abrahams and Robertson, *Acta Cryst.*, 1948, **1**, 252.
[13] Kumler and Strait, *J. Amer. Chem. Soc.*, 1943, **65**, 2349.

---

951. *Infrared Spectra of Natural Products. Part VI.* The Characterization of Equatorial and Axial 3-Hydroxyl Groups in Triterpenoids.*

By (Miss) I. L. Allsop, A. R. H. Cole, D. E. White, and R. L. S. Willix.

A significant difference in the stretching frequency of equatorial (3629—3630 cm.$^{-1}$) and axial (3637—3639 cm.$^{-1}$) 3-hydroxyl groups in triterpenoids is described, and used to determine the configuration of a hydroxyl group in a new compound. Bands in the 950—1200 cm.$^{-1}$ region are correlated with the stereochemistry of the 3-hydroxy-triterpenoids and their acetates. The intense band near 1240 cm.$^{-1}$ in the acetate spectra is "simple" both for equatorial and axial groups, in contrast to the steroids, where axial acetates give a complex system of bands between 1220 and 1260 cm.$^{-1}$.

The correlation of infrared absorption frequencies with equatorial or axial orientation of hydroxyl and acetoxyl groups in steroids and simpler cyclic compounds [1-9] has provided a simple method of determining the orientation of these groups in new compounds or in those whose stereochemistry has not previously been fully elucidated.[10,11] The present paper extends these measurements to the tetracyclic and pentacyclic triterpenoids, and draws special attention to the stretching frequencies of the hydroxyl groups.

Hydroxyl Compounds.—In the steroids and decalols, equatorial hydroxyl groups are characterized by a strong band near 1040 cm.$^{-1}$, and axial groups by absorption at somewhat lower frequencies (1000—1034 cm.$^{-1}$). This absorption is due to a stretching vibration of the C–O bond, and the difference in frequency is attributed [2,9] to a difference in the

* Part V, *J.*, 1956, 1007.

[1] Rosenkrantz, Milhorat, and Farber, *J. Biol. Chem.*, 1952, **195**, 509.
[2] Cole, Jones, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 5571.
[3] Fürst, Kuhn, Scotoni, and Günthard, *Helv. Chim. Acta*, 1952, **35**, 951.
[4] Rosenkrantz and Skogstrom, *J. Amer. Chem. Soc.*, 1955, **77**, 2237.
[5] Dauben, Holger, and Freeman, *ibid.*, 1952, **74**, 5206.
[6] Hirschmann, *ibid.*, 1952, **74**, 5357.
[7] Rosenkrantz and Zablow, *ibid.*, 1953, **75**, 903.
[8] Jones and Herling, *ibid.*, 1956, **78**, 1152.
[9] Cole, *Fortschr. Chem. org. Naturstoffe*, 1956, **13**, 1.
[10] Cole, *J.*, 1952, 4969.
[11] Aebi, Barton, and Lindsay, *Chem. and Ind.*, 1953, 748.

direction of motion of the carbon atom relative to the *cyclo*hexane ring, with a lower restoring force in the axial compounds. The steroid measurements covered a number of different systems in which the A/B ring junction is *cis* (testane and lumistane series) and *trans* (androstane series), but the compounds available for this study of the triterpenoids all have the *trans* A/B ring junction. Hence the 3α-hydroxyl groups are axial and the 3β-equatorial.

The frequencies and peak intensities of the hydroxyl stretching band and the intense peaks between 950 and 1070 cm.$^{-1}$ for six epimeric pairs of 3-hydroxy-triterpenoids are given in Table 1 and typical examples of the spectra are shown in the Figure.

TABLE 1. *Frequencies (cm.$^{-1}$) and peak intensities (in parentheses) of* (i) *the* OH *stretching band (in carbon tetrachloride) and* (ii) *the intense bands in the range* 950—1070 *cm.$^{-1}$ (in carbon disulphide) for* 3α- *and* 3β-*hydroxy-triterpenoids.*

	(i)	(ii)
Equatorial		
Urs-12-en-3β-ol (α-amyrin)	3630 (48)	1042 (129), 1026 (129), 993 (133)
Olean-12-en-3β-ol (β-amyrin)	3629 (49)	1042 * 1029 (129), 995 (104)
Lup-20(29)-en-3β-ol (lupeol)	3630 (51)	1040 (131), 1013 (90), 983 (80)
Methyl 3β-hydroxylup-20(29)-en-28-oate (methyl betulate)	3629 (54)	1042 (163), 1031 (138), 983 (138)
9 : 19-*cyclo*Lanost-24-en-3β-ol (*cyclo*artenol)	3630 (56)	1045 (98) {1020 (114), 1004 (101)} 989 (87)
Lanost-8-en-3β-ol (dihydrolanosterol)	3630 (51)	1025 (233)
Axial		
Urs-12-en-3α-ol (*epi*-α-amyrin)	3638	1068 (106), 1057 (80), 990 (119)
Olean-12-en-3α-ol (*epi*-β-amyrin)	3638 (60)	1069 (118) 992 (93)
Lup-20(29)-en-3α-ol (*epi*lupeol)	3639 (61)	1065 (138) 988 (140)
Methyl 3α-hydroxylup-20(29)-en-28-oate	3637 (60)	1066 (100) 989 (182)
9 : 19-*cyclo*Lanost-24-en-3α-ol	3638 (56)	1065 (97), 1047 (97), 969 (93)
Lanost-8-en-3α-ol	3638 (56)	1063 (91) 975 (91)

* Weak band on side of 1029 cm.$^{-1}$ peak.

Hydroxyl stretching frequencies. Careful measurements of the hydroxyl absorption band indicate that axial groups absorb at a higher frequency (3637—3639 cm.$^{-1}$) than equatorial groups (3629—3630 cm.$^{-1}$). The difference in frequency is small, but is easily detectable when a calcium fluoride or lithium fluoride prism is used in a spectrometer equipped with a thermostat to eliminate changes in prism dispersion, and in single-beam instruments the weak water-vapour spectrum in the background provides a very useful internal calibration. There is virtually no variation of frequency among the six compounds of each type, and this information should prove useful in determining the orientation of 3-hydroxyl groups in new triterpenoids. No similar measurements have been reported on steroids or simpler *cyclo*hexane compounds. The difference is not quite so marked in the menthols,[12] but in these, too, the axial frequency (3632 cm.$^{-1}$) is higher than the equatorial (3627—3628 cm.$^{-1}$).

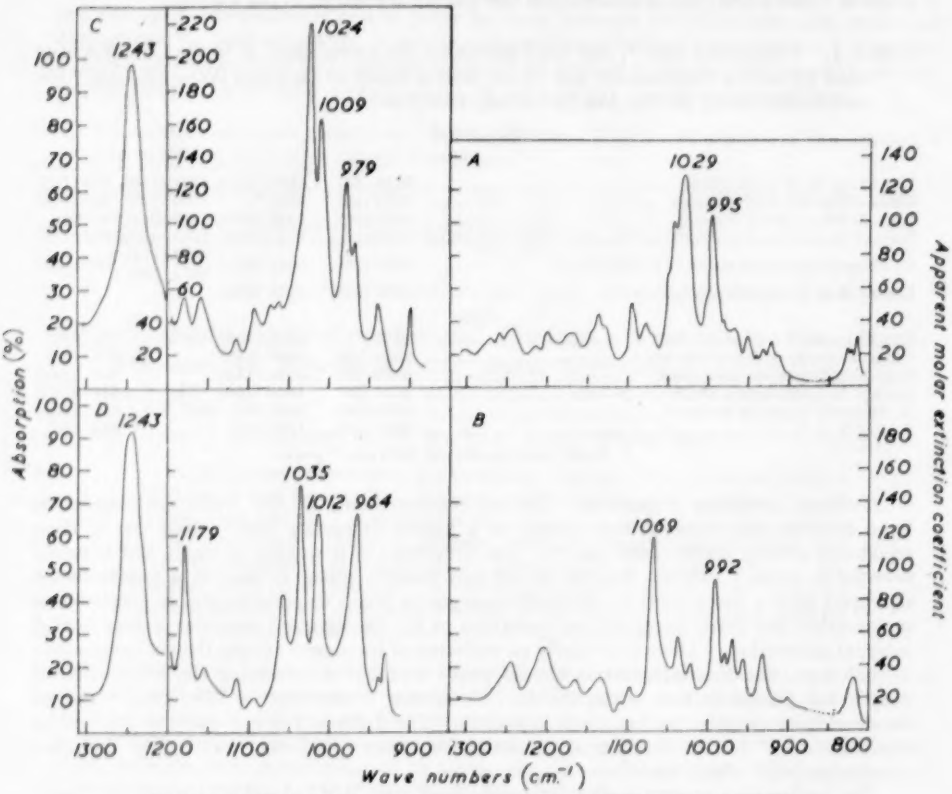
The hydroxyl apparent molar extinction coefficient [13,14] [$\varepsilon = (1/cl) \log_{10} (I_0/I)$] has a peak value of approximately 50. This figure can be used for determining the number of hydroxyl groups in an unknown compound, but it should be remembered that maximum extinction coefficients are only additive when the groups absorb at exactly the same frequency and for best results absorption areas should be used. The solutions used in this work were all sufficiently dilute to prevent intermolecular hydrogen bonding.

Bands in the C–O *stretching region.* The spectra in the range 950—1070 cm.$^{-1}$ are somewhat more complex than those of 3-epimeric sterols. The equatorial 3-hydroxy-triterpenoids usually have three intense bands, near 1040, 1025, and 990 cm.$^{-1}$, although lanost-8-en-3β-ol resembles the sterols in having only one intense band in this region (1025 cm.$^{-1}$). *cyclo*Artenol and *cyclo*artanol have an additional band at 1004 and 1012 cm.$^{-1}$, respectively. With inversion to the axial configuration the band near 990 cm.$^{-1}$ remains

[12] Cole and Jefferies, *J.*, 1956, 4391.
[13] Ramsay, *J. Amer. Chem. Soc.*, 1952, **74**, 72.
[14] Smith and Creitz, *J. Res. Nat. Bur. Stand.*, 1951, **46**, 145.

in the same position, but the other intense absorption moves to 1063—1069 cm.$^{-1}$. Thus it appears that absorption at either 1025 or 1040 cm.$^{-1}$ (equatorial) and 1065 cm.$^{-1}$ (axial) must be identified as that due to the stretching of the C–O bond. This increase in frequency with change from equatorial to axial orientation is opposite to that found for the sterols and must be due to the presence of the *gem*-dimethyl group at $C_{(4)}$. Indeed, the increase

Infrared spectra of stereoisomeric 3-hydroxy- and 3-acetoxy-triterpenoids (CS_2 *solutions*; NaCl *prism, double-pass*). *The percent absorption scale applies only to the bands at* 1243 cm.$^{-1}$.



(A) *Olean-12-en-3β-ol* (*β-amyrin*).
(B) *Olean-12-en-3α-ol* (epi-*β-amyrin*).
(C) *Lanost-8-en-3β-yl acetate.*
(D) *Lanost-8-en-3α-yl acetate.*

in complexity of the spectra in this region compared with those of the sterols is probably due to the increase in mass of this neighbouring centre which may lead to vibrational resonance. It is likely that the fairly intense band near 990 cm.$^{-1}$ is due to a C–C vibration involving this part of the molecule, since Jones, Katzenellenbogen, and Dobriner [15] have shown that in the spectra of the steroidal sapogenins all the intense bands in this region are due to vibrations of bonds near the oxygenated groups.

For determination of the orientation of the 3-hydroxyl group in a triterpenoid the bands at 1065 cm.$^{-1}$ (axial) and 1025—1040 cm.$^{-1}$ (equatorial) are sufficiently specific to leave little doubt. This absorption lies in the range covered by the sodium chloride prism and, where only this prism is available, will be easier to measure than the difference

[15] Jones, Katzenellenbogen, and Dobriner, *J. Amer. Chem. Soc.*, 1953, **75**, 158.

in hydroxyl stretching absorption described above. Other oxygenated groups (*e.g.*, acetates, see below) often cause fairly strong absorption in this region, but the results for methyl betulate and its $C_{(3)}$-epimer indicate that the two types of hydroxyl orientation can be identified in the presence of a methyl ester group.

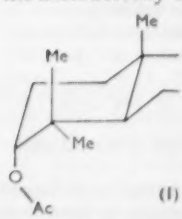
Acetates.—Table 2 gives the frequencies of the intense absorption bands of the epimeric acetates in the range 950—1250 cm.$^{-1}$, and typical spectra are shown in the Figure.

TABLE 2. *Frequencies (cm.$^{-1}$) and peak intensities (in parentheses) of the intense bands in the range 950—1250 cm.$^{-1}$ for 3α- and 3β-acetoxy-triterpenoids (in carbon disulphide). The bands near 1240 cm.$^{-1}$ are all "simple."*

	Equatorial		
Urs-12-en-3β-yl acetate	1240		1023 (223), 1003 (136), 982 (138)
Olean-12-en-3β-yl acetate	1243		1025 (312), 1003 (166), 984 (166)
Lup-20(29)-en-3β-yl acetate	1243		1026 (196), 1015 (157), 978 (200)
Methyl 3β-acetoxylup-20(29)-en-28-oate	1245		1025 (198), 1009 (127), 978 (224)
9 : 19-*cyclo*Lanost-24-en-3β-yl acetate	1243		{1039 (132)} {1023 (183)} 977 (124)
Lanost-8-en-3β-yl acetate	1243		1024 (220), 1009 (162), 979 (124)
	Axial		
Urs-12-en-3α-yl acetate	1243	1174 (137)	{1052 (105)} {1034 (110)} 1016 (120), 988 (170)
Olean-12-en-3α-yl acetate	1243	1183 (133)	1035 (128), 1016 (121), 986 (123)
Lup-20(29)-en-3α-yl acetate	1243	1180 (133)	1033 (150), 1012 (131), 981 (165)
Methyl 3α-acetoxylup-20(29)-en-28-oate	1245	~1180	1033 (156), 1014 (146), 982 (238)
9 : 19-*cyclo*Lanost-24-en-3α-yl acetate	1243	{1175 (95)} {1195 (95)}	1040 (216), 1016 (104), 974 (113)
Lanost-8-en-3α-yl acetate	1243	1179 (115)	1035 (151), 1012 (133), 964 (133)

Absorption near 1240 *cm.*$^{-1}$. The absorption due to one of the C–O stretching vibrations of the acetate group lies near 1240 cm.$^{-1}$. In acetoxy-steroids with the acetoxy-group in ring A [3,4,16] this band is usually single and symmetrical for equatorial groups ("simple") while the absorption due to axial groups consists of a system of two or three peaks between 1220 and 1260 cm.$^{-1}$ ("complex"). An exception to this scheme is cholestan-4α-yl acetate [3] which exhibits complex absorption (1236 and 1247 cm.$^{-1}$).

All the 3-acetoxy-triterpenoids examined exhibit "simple" absorption at 1240—1245 cm.$^{-1}$ regardless of configuration. The lack of complexity of the spectra of the axial group must be attributed to the presence of the $C_{(4)}$-*gem*-dimethyl group since this is the only point of difference between the triterpenoids and steroids in this part of the molecule. Intensity studies at different temperatures led Jones *et al.*[16] to suggest that the "complex" spectra may be due to the presence of rotational isomers. The $C_{(4)}$-methyl groups should not interfere with rotation about the single bonds of the acetate group since they are oriented in different directions (I) and the explanation of the "complex" absorption of the axial acetoxy-steroids may lie in vibrational resonance rather than rotational isomerism. Such resonance could be upset by the increased mass of the $C_{(4)}$ centre in triterpenoids.



(I)

The axial acetates have a fairly intense band ($\varepsilon \sim 130$) near 1180 cm.$^{-1}$ while none of the equatorial acetates has bands with $\varepsilon > 60$ at this position. This band is too far away from the peak at 1240 cm.$^{-1}$ to be looked upon as a component of a "complex" system, but should be useful in conjunction with the other spectral regions in determining orientation. With *epi-cyclo*artenyl acetate this absorption is split into two bands of equal intensity ($\varepsilon = 95$) at 1175 and 1195 cm.$^{-1}$. Very strong absorption in this region by the methyl ester group interfered with observation of this band in the spectrum of methyl 3α-acetoxy-lup-20(29)-en-28-oate, although the absorption of the axial compound at 1180 cm.$^{-1}$ is more intense than that of the equatorial.

Absorption near 1000 *cm.*$^{-1}$. Acetates also have fairly intense absorption in the region

[16] Jones, Humphries, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1951, **73**, 3215.

960—1040 cm.$^{-1}$ which varies systematically according to the orientation of the group. Equatorial triterpenoid acetates are characterized by a band at 1024—1025 cm.$^{-1}$, to be found at 1033—1035 cm.$^{-1}$ with the axial compound. The shift of this frequency to a higher value for the axial compounds parallels the absorption of the hydroxyl compounds described above, and is again opposite to that described for the steroids.[4,8] Other strong bands are present at 1003—1016 and 964—988 cm.$^{-1}$ but the frequencies of these are not so clearly related to the stereochemistry.

Table 3 summarizes data useful for determining the orientation of 3-hydroxyl groups in triterpenoids.

TABLE 3. *Summary of band frequencies (cm.$^{-1}$) which are characteristic of equatorial and axial hydroxyl and acetoxyl groups at position 3 in triterpenoids.*

	Hydroxyl groups	Acetoxyl groups
Equatorial	3629—3630,* 1013—1031,† 1040—1045 †	1023—1026 †
Axial	3637—3639,* 1063—1068 †	1174—1183,† 1033—1040 †

* Carbon tetrachloride solution. † Carbon disulphide solution.

Application.—The 3-hydroxyl group of dimethyl melaleucate [17] absorbs at 3629 cm.$^{-1}$, while that of its $C_{(3)}$-epimer obtained by oxidation to the ketone and reduction with aluminium *iso*propoxide absorbs at 3636 cm.$^{-1}$. This indicates that the hydroxyl group in the natural product has the β (or equatorial) configuration. The fairly strong absorption of the two methoxycarbonyl groups makes observations in the range 1000—1070 cm.$^{-1}$ rather uncertain, but methyl melaleucate absorbs more strongly near 1040 cm.$^{-1}$ and its $C_{(3)}$-epimer more strongly near 1065 cm.$^{-1}$ which is in accord with Table 1.

EXPERIMENTAL

The infrared spectrometer has been described previously.[18] Solutions in carbon tetrachloride (3-mm. cell; CaF_2 prism) were used for measurement of the hydroxyl stretching frequency and solutions in carbon disulphide (1·3 mm. cell; NaCl prism) for measurements in the region 950—1250 cm.$^{-1}$. Frequencies are accurate to ±1 cm.$^{-1}$ throughout the regions studied, and intensity measurements to ±5%. The effective slit widths at 3630, 1240, and 1000 cm.$^{-1}$ are respectively 6, 4, and 3 cm.$^{-1}$.

Rotations were observed in chloroform solution in 1 dm. tubes. Light petroleum refers to the fraction, b. p. 40—60°. B.D.H. alumina was used for chromatography after being neutralized with nitric acid, washed and standardized.[19] Analyses are by Dr. K. Zimmermann, Melbourne, on samples dried at 100°/0·1 mm. for at least 24 hr. Melting points were determined in evacuated capillaries and are corrected.

Urs-12-en-3α-ol (epi-α-*Amyrin*).—Urs-12-en-3-one (α-amyrenone) (2·0 g.) was added to a solution of aluminium *iso*propoxide (2·5 g.) in dry propan-2-ol (25 ml.). The mixture was distilled slowly until the distillate was free from acetone (*ca.* 4 hr.), the volume being maintained by adding propan-2-ol when necessary. Finally the solvent was removed *in vacuo* and the residue washed with dilute hydrochloric acid, 5% sodium hydrogen carbonate solution, and water. *Urs-12-en-3α-ol* (0·54 g.; m. p. 134—137°) was obtained from the crude product in fractions 8—13 (200 ml. each) on elution from alumina (50 g.; activity II) by light petroleum–benzene (9 : 1). Crystallization from aqueous acetone afforded fine needles, m. p. 138°; $[\alpha]_D$ +75° (*c*, 0·98) (Found: C, 84·3; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). Treatment with acetic anhydride and pyridine afforded urs-12-en-3α-yl acetate, m. p. 135°, $[\alpha]_D$ +40° (*c*, 0·72).[20]

From fractions 21—23 (0·44 g.) of the chromatogram α-amyrin, m. p. 186° (from ethanol), was obtained.

Lup-20(29)-en-3α-ol (epi*Lupeol*).—Lup-20(29)-en-3-one was prepared by oxidation of lupeol with 8N-chromium trioxide in acetone,[21] and on reduction and chromatography as described above afforded *lup-20(29)-en-3α-ol* in fractions 2—6 eluted by benzene (each 50 ml.). It formed prisms, m. p. 202·5°, $[\alpha]_D$ +15° (*c*, 0·94), from acetone (Found: C, 84·6; H, 12·1. $C_{30}H_{50}O$

[17] Arthur, Cole, Thieberg, and White, *Chem. and Ind.*, 1956, 926.
[18] Cole and Thornton, *J.*, 1956, 1007.
[19] Brockmann and Schodder, *Ber.*, 1941, **74**, 73.
[20] Büchi, Jeger, and Ruzicka, *Helv. Chim. Acta*, 1946, **29**, 442.
[21] Curtis, Heilbron, Jones, and Woods, *J.*, 1953, 457.

requires C, 84·4; H, 11·8%). The *acetate*, m. p. 163°, $[\alpha]_D$ −1° (*c*, 0·99), formed plates from ether–methanol (Found: C, 81·7; H, 11·3. $C_{32}H_{52}O_3$ requires C, 82·0; H, 11·2%).

From fractions 14—21, lupeol, m. p. 215°, $[\alpha]_D$ +29°, was obtained.

Methyl 3α-Hydroxylup-20(29)-en-28-oate.—Methyl betulonate (prepared with chromium trioxide in acetone [21]) was reduced and chromatographed as above and afforded, in fractions 8—14 eluted from alumina (activity III) with light petroleum–benzene (1 : 1), *methyl 3α-hydroxylup-20(29)-en-28-oate* which formed needles, m. p. 225·5°, $[\alpha]_D$ −13° (*c*, 0·97), from methanol (Found: C, 79·0; H, 10·8. $C_{31}H_{50}O_3$ requires C, 79·15; H, 10·6%). With acetic anhydride and pyridine this afforded *methyl 3α-acetoxylup-20(29)-en-28-oate* which formed needles, m. p. 227°, $[\alpha]_D$ −24° (*c*, 0·92), from aqueous methanol (Found: C, 77·3; H, 10·2. $C_{33}H_{52}O_4$ requires C, 77·3; H, 10·2%).

From fractions 23—29 of the chromatography methyl betulate, m. p. 228°, $[\alpha]_D$ +5°, was obtained.

9 : 19-cyclo*Lanost-24-en-3α-ol.*—*cyclo*Artenone was reduced by the procedure described above and afforded 9 : 19-cyclo*lanost-24-en-3α-ol*, in fractions 6—9 eluted with benzene (each 50 ml.) from alumina (activity II). It formed needles, m. p. 84°, $[\alpha]_D$ +39° (*c*, 0·98), from methanol (Found: C, 84·6; H, 11·9. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8%). With acetic anhydride and pyridine it afforded 9 : 19-cyclo*lanost-24-en-3α-yl acetate*, m. p. 123°, $[\alpha]_D$ +5·5° (*c*, 0·9), which formed prisms from chloroform–methanol (Found: C, 82·2; H, 11·3. $C_{32}H_{52}O_2$ requires C, 82·0; H, 11·2%).

From fractions 13—15, *cyclo*artenol, m. p. 115°, was obtained.

Lanost-8-en-3α-ol.—Reduction of lanost-8-en-3-one as described above afforded lanost-8-en-3α-ol, in fractions 6—13 eluted with light petroleum–benzene from alumina (activity II). It formed minute prisms, m. p. 139°, $[\alpha]_D$ +49° (*c*, 0·93), from acetone–methanol, and yielded an acetate, m. p. 167·5°, $[\alpha]_D$ −1° (*c*, 0·96) (in good agreement with Marker and Wittle [22]).

The infrared spectrometer was purchased through a generous grant from the Nuffield Foundation, to whom one of us (A. R. H. C.) is indebted for a Fellowship. We thank Professor D. H. R. Barton, Dr. W. Klyne, Dr. H. J. Rodda, Dr. R. G. Curtis, and Dr. R. M. Gascoigne who supplied some of the compounds used and Professor G. L. Adamson for a generous gift of Manila elemi resin.

Department of Chemistry, University of W. Australia, Nedlands, W. Australia. [*Received, July 16th*, 1956.]

[22] Marker and Wittle, *J. Amer. Chem. Soc.*, 1937, **59**, 2289.

---

952. *Nucleotides. Part XXXIX.* 5′-Deoxy-5′-iodo-O²:2′-cyclouridine: an X-Ray Crystallographic Study.*

By D. M. Brown, W. Cochran, E. H. Medlin, and S. Varadarajan.

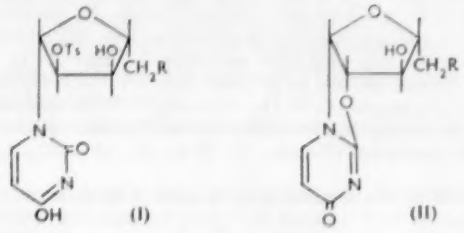
The structure of *O²:2′-cyclo*uridine [1] is confirmed by an *X*-ray crystallographic examination of its 5′-deoxy-5′-iodo-derivative, prepared by the action of methanolic ammonia on 5′-deoxy-5′-iodo-2′-*O*-toluene-*p*-sulphonyluridine. Iodo*cyclo*uridine and *O²:2′-cyclo*uridine are related by conversion into 3-β-D-arabofuranosyluracil.

In earlier experiments [1] related to the orientation of the phosphate residue in uridylic acids *a* and *b*, uridine-5′ acetate and a uridine-*x*:5′ diacetate were converted into mono-toluene-*p*-sulphonyl derivatives. On attempted deacetylation with methanolic ammonia both toluene-*p*-sulphonyl derivatives were converted into an anhydrouridine. The product was formulated as a *cyclo*uridine since it was similar to other known *cyclo*nucleosides in its properties,[2,3,4] and structure (II; R = OH) was assigned to it on the grounds of quantitative acid hydrolysis into 3-β-D-arabofuranosyluracil, shown to be identical with

* Part XXXVIII, *J.*, 1956, 3459.

[1] Brown, Todd, and Varadarajan, *J.*, 1956, 2388.
[2] Clark, Todd, and Zussman, *J.*, 1951, 2952.
[3] Michelson and Todd, *J.*, 1955, 816.
[4] Brown, Todd, and Varadarajan, following paper.

the naturally occurring nucleoside spongouridine.[5] The original toluene-*p*-sulphonyl derivatives were therefore formulated as the 2′-isomers.



Confirmation of the position of the new ring in (II; R = OH) was sought by *X*-ray crystallography. To facilitate this, compounds related to (II; R = OH) carrying heavy

FIG. 1*a*. *Electron density projected on* (010). *Light atom contours at* 2eÅ^{-2} *intervals, with the first contour at* 0·75eÅ^{-2}. *Iodine contours are drawn at* 10, 20, 40, 60, 80, 90eÅ^{-2}.

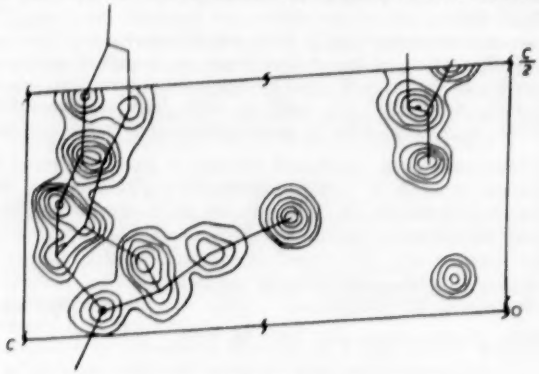
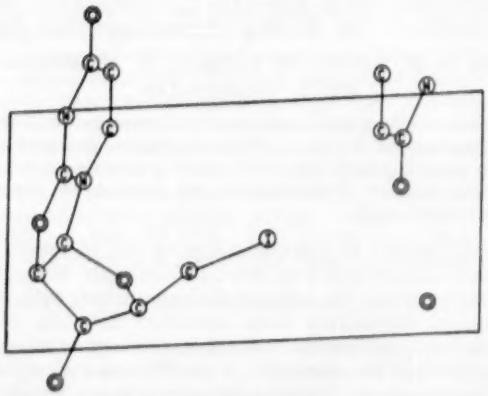


FIG. 1*b*.



atoms were prepared. 2′ : 3′-*O*-*iso*Propylideneuridine [6] was converted through the 5′-*O*-toluene-*p*-sulphonyl- and 5′-bromo-5′-deoxy-derivatives into 5′-bromo-5′-deoxyuridine. This yielded the 2′-toluene-*p*-sulphonyl derivative (I; R = Br) which was

[5] Bergmann and Burke, *J. Org. Chem.*, 1955, **20**, 1501.
[6] Levene and Tipson, *J. Biol. Chem.*, 1934, **106**, 113.

converted into the bromo-compound (II; R = Br) by methanolic ammonia. By a similar series of reactions (II; R = I) was prepared.[4] The bromo- and iodo-*cyclo*nucleosides were both closely similar to *O*^{2} : 2′-*cyclo*uridine (II; R = OH) in their ultraviolet spectra and infrared absorption in the carbonyl region.[1,4] The iodo-compound (II; R = I) was more amenable to crystallographic analysis and its structural relation to (II; R = OH) was established by conversion into spongouridine by acid hydrolysis followed by treatment with aqueous silver acetate and acetic acid.[4]

Direct evidence for structure (II; R = I) is provided by the results of *X*-ray crystallographic examination. Oscillation and Weissenberg photographs gave the following information about the unit cell: $a = 9{\cdot}96$, $b = 5{\cdot}61$, $c = 10{\cdot}02$ Å, $\beta = 93°\ 0'$; space group $P2_1$. Fig. 1*a* shows the electron-density projection on (010) with the asymmetric unit superimposed, and Fig. 1*b* the molecular appearance. The reliability index for this projection is 11·5%. The new ring is shown to be formed between O^2 and $C_{(2')}$ and supporting evidence is given by the deviation of the glycosidic linkage from the direction N^3–$C_{(6)}$. In addition, the puckering of the furanose ring brings $C_{(2')}$ out of the plane on the side opposite to the $C_{(2')}$–O^2 bond. The bonds $C_{(3')}$–O and $C_{(1')}$–N^3 are in the expected *trans*-relation. It is clear that inversion at $C_{(2')}$ to the *arabo*-configuration occurs during formation of the *cyclo*nucleoside. It follows from the chemical relation established that the parent *cyclo*nucleoside [1] is correctly described as *O*^{2} : 2′-*cyclo*uridine (II; R = OH).

Generalised projections are being used to establish in greater detail the stereochemistry of (II; R = I) and intermolecular bonds and contacts.

Experimental

*5′-Deoxy-5′-iodo-2′-O-toluene-*p*-sulphonyluridine.*—Toluene-*p*-sulphonyl chloride (0·59 g.; 1·1 mol.) was added to a solution of 5′-deoxy-5′-iodouridine [4] (1·0 g.) in dry pyridine (20 c.c.). After 15 hr. at room temperature the mixture was added to cold water (150 c.c.), and the sticky red product washed with water by decantation. Trituration with ethanol gave the colourless *toluene-*p*-sulphonyl* derivative as fine needles (0·32 g.) (from ethanol), m. p. 168—169° (Found: C, 37·8; H, 3·4; N, 5·7. $C_{16}H_{17}O_7N_2IS$ requires C, 37·8; H, 3·9; N, 5·5%). Light absorption in 95% EtOH: $\lambda_{max.}$ 259, 227 mμ (ε 9280, 13,900); $\lambda_{min.}$ 243, 215 mμ (ε 6430, 11,800).

*5′-Deoxy-5′-iodo-*O^2 : 2′-cyclo*uridine.*—The toluenesulphonate (0·6 g.) in methanol (300 c.c.) was treated with an equal volume of saturated methanolic ammonia. After 12 hr. solvent was removed, the residue triturated with ethanol (5 c.c.), and undissolved ammonium toluene-*p*-sulphonate filtered off. The filtrate was evaporated and the residue purified by counter-current distribution, the ethyl acetate–water system (20·5 c.c. phase; 100 transfers) being used. The contents of tubes 8—24 were mixed and evaporated to dryness and the crystalline residue was recrystallised from 95% ethanol. *5′-Deoxy-5′-iodo-*O^2 : 2′-cyclo*uridine* separated in rods (0·1 g), m. p. 194—195° (decomp.) (Found: C, 33·7; H, 3·2; N, 8·6; I, 36·9. $C_9H_9O_4N_2I$ requires C, 32·2; H, 2·7; N, 8·3; I, 37·7%). Light absorption in water: $\lambda_{max.}$ 249, 225 mμ (ε 8690, 8400); $\lambda_{min.}$ 235, 210 mμ (ε 7320, 4890). Infrared absorption bands in the carbonyl region were at 1613 and 1660 cm.$^{-1}$.

3-β-D-*Arabofuranosyluracil* (*Spongouridine*).—A solution of 5′-deoxy-5′-iodo-*O*^{2} : 2′-*cyclo*uridine (0·25 g.) in 0·1N-sulphuric acid (15 c.c.) was heated at 100° for 1 hr., then cooled and passed through a column (10 × 1·5 in.) of Amberlite IR-4B resin (OH form). The column was washed with distilled water (450 c.c.) and percolate and washings were evaporated to dryness under reduced pressure. The residue of 5′-deoxy-5′-iodospongouridine was heated at 100° with silver acetate (1·0 g.) in water (35 c.c.) for 15 min. After filtration through Hyflo Supercel, acetic acid (15 c.c.) was added, and the solution was heated at 100° for a further 15 min. and cooled. Silver ions were removed by hydrogen sulphide and, after being filtered through Supercel, the solution was evaporated. Crystallisation of the residue from dry methanol gave spongouridine (63 mg.) as prisms, m. p. 220—221° alone or in admixture with an authentic specimen.[1]

5′-Bromo-5′-deoxy-2′ : 3′-O-isopropylideneuridine.—A solution of 2′ : 3′-*O-iso*propylidene-5′-*O*-toluene-*p*-sulphonyluridine [6] (8·5 g.) and anhydrous lithium bromide (10 g.) in dry acetone (120 c.c.) was heated for 2 hr. at 100° in an autoclave. The solvent was removed, water added to the residue, and the insoluble *bromo*-compound collected. It formed rectangular rods (6·0 g.), m. p. 184—186°, from ethanol (charcoal) (Found: C, 42·3; H, 4·5; N, 8·4; Br, 23·3. $C_{12}H_{15}O_5N_2Br$ requires C, 41·5; H, 4·4; N, 8·1; Br, 23·0%).

5'-Bromo-5'-deoxyuridine.—The *iso*propylidene derivative (1·46 g.) was dissolved in anhydrous formic acid (20 c.c.) and after 3 hr. at room temperature the solution was evaporated to dryness. Ethanol (35 c.c.) was added and distilled off under reduced pressure to remove last traces of formic acid. *5'-Bromo-5'-deoxyuridine* separated from ethanol in needles or thin plates (0·83 g.), m. p. 182—184° (Found: C, 35·7; H, 3·9; N, 9·0. $C_9H_{11}O_5N_2Br$ requires C, 35·2; H, 3·6; N, 9·1%).

5'-Bromo-5'-deoxy-2'-O-toluene-p-sulphonyluridine.—5'-Bromo-5'-deoxyuridine (3·7 g.) and toluene-*p*-sulphonyl chloride (2·3 g.; 1·1 mol.) were dissolved in dry pyridine (25 c.c.), and the solution was set aside overnight. When this was added to water (250 c.c.) a gum separated. Trituration with methanol gave a solid (2·7 g.) which was then crystallised from methanol. The 2'-O-*toluene*-p-*sulphonyl* derivative formed thick plates, m. p. 162—163° (Found: C, 42·4; H, 3·8; N, 6·1. $C_{16}H_{17}O_7N_2BrS$ requires C, 41·7; H, 3·7; N, 6·1%).

5'-Bromo-5'-deoxy-O²:2'-cyclouridine.—5'-Bromo-5'-deoxy-2'-*O*-toluene-*p*-sulphonyluridine (2·1 g.) was dissolved in half-saturated methanolic ammonia (200 c.c.). After 12 hr. the solution was evaporated to dryness and the residue treated with cold ethanol (10 c.c.). Ammonium toluene-*p*-sulphonate was filtered off and the filtrate was evaporated. The residue was purified by counter-current distribution (20·5 c.c. phase; 100 transfers), the ethyl acetate–water system being used. The contents of tubes 6—16 were pooled and evaporated, and the residue was crystallised from ethanol. *5'-Bromo-5'-deoxy-O²:2'-cyclouridine* formed pale yellow stout prisms (0·53 g.), m. p. 185—186° (Found: C, 38·1; H, 3·1; N, 9·7. $C_9H_9O_4N_2Br$ requires C, 37·4; H, 3·1; N, 9·7%). Light absorption in water: $\lambda_{max.}$ 247, 225 mμ (ε 7940, 9450); $\lambda_{min.}$ 238, 210 mμ (ε 7500, 6070). Infrared absorption bands in the carbonyl region were at 1613 and 1662 cm.$^{-1}$.

We thank Sir Alexander Todd, F.R.S., for his interest in this work. Grateful acknowledgment is made of an Overseas Scholarship of the Royal Commission for the Exhibition of 1851 and a Travel Grant of the British Council awarded to one of us (S. V.).

UNIVERSITY CHEMICAL LABORATORY
AND CAVENDISH LABORATORY, CAMBRIDGE. [*Received, July 26th*, 1956.]

---

953. *The Equilibrium in the System: Water–6-Hexanolactam (ε-Caprolactam).*

By A. B. MEGGY.

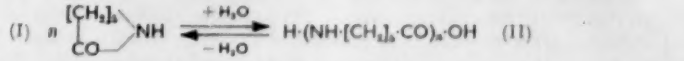
Equations are calculated for the activity coefficients of water and polymer in the system water–6-hexanolactam. The equations are expressed in terms of the apparent equilibrium constants and the mol. fractions of water and lactam, and can be evaluated from published data. From the values obtained a composition–temperature diagram for the system can be constructed, showing lines of equal degree of polymerization, of equal partial pressure of water, and of equal lactam content, from 200° to 300°.

IN a previous paper [1] the polymerization of 6-hexanolactam (ε-caprolactam) to a linear polyamide was discussed. Recent publications [2-13] provide experimental material for a fresh analysis of the problem.

In the presence of water or of alkali metals or their hydroxides, 6-hexanolactam (I)

[1] Meggy, *J.*, 1953, 796.
[2] Wiloth, *Makromol. Chem.*, 1954, **14**, 156.
[3] *Idem, ibid.*, 1954, **15**, 98.
[4] *Idem, ibid.*, p. 104.
[5] *Idem, Z. phys. Chem.*, 1955, **5**, 66.
[6] *Idem, Koll. Z.*, 1955, **143**, 129.
[7] *Idem, ibid.*, p. 138.
[8] Hermans, *J. Appl. Chem.*, 1955, **5**, 493.
[9] Van Velden, van der Want, Heikens, Kruissink, Hermans, and Staveman, *Rec. Trav. chim.*, 1955, **74**, 1376.
[10] Yumato, *Bull. Chem. Soc. Japan*, 1955, **28**, 94, 101.
[11] Skuratov, Stipikheev, and Kanarskaya, *Faserforsch. u. Textiltechnik*, 1953, **4**, 390.
[12] Ludwig and Froeber, *ibid.*, 1954, **5**, 277.
[13] Matthes, *Makromol. Chem.*, 1951, **5**, 198; *Chem. Technik*, 1952, 129.

polymerizes to a linear polyamide (II) of 6-aminohexanoic acid. The molten polymer can be spun into fibres (called nylon-6). In the technical process water is the effective catalyst.[8]



(I) (II)

The degree of polymerization of the polymer is determined by the equilibrium :

$$x\text{-mer} + y\text{-mer} = (x + y)\text{-mer} + H_2O$$
$$K_1 = (H_2O)([x + y]\text{-mer})/(x\text{-mer})(y\text{-mer}) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The polymerization does not go to completion; 5—10% of the lactam remains in the equilibrium mixture. The lactam may be regarded as being in equilibrium with 6-aminohexanoic acid and water :

$$K_2 = (\text{lactam})(H_2O)/(6\text{-aminohexanoic acid}) \quad . \quad . \quad . \quad (2)$$

Lactam is also in equilibrium with polymer :

$$\text{lactam} + x\text{-mer} = (x + 1)\text{-mer}$$
$$K_3 = ([x + 1]\text{-mer})/(x\text{-mer})(\text{lactam}) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

In order to develop these equations it is necessary to make two assumptions : (*a*) In eqn. (1), the value of K_1 at any temperature is the same for all values of x and y, including x or $y = 1$. This is the principle of " equal reactivity of all groups " postulated by Flory.[14] If this principle applies, the mol. fraction of the x-mer in a polymer having a number average degree of polymerization n, is $(1 - 1/n)^{x-1}/n^2$. This expression has been tested experimentally, with satisfactory agreement, for poly-6-aminohexanoic acid [2] and for poly(hexamethyleneadipamide).[15] (*b*) In the presence of a diluent, if a_2 is the activity of the whole polymer, and m_x is the mol. fraction of the x-mer in the polymer, then the activity of the x-mer is a_2m_x. This is equivalent to assuming that the interaction between a diluent molecule and the polymer is independent of the length of the polymer chain. This might be expected to be valid for ranges where the length of the polymer chain was considerably greater than the " segment " of the chain which was equivalent to a diluent molecule under the Flory–Huggins lattice theory.[16] It will be shown later that there is evidence that the size of the polymer " segment " in the system polyaminohexanoic acid–water is less than one repeating unit of the polymer, so that the above assumption may be expected to hold down to quite low degrees of polymerization.

On the basis of these two assumptions it is possible to develop eqn. (1)—(3). Let the activity of water in the system be a_1, that of the polymer be a_2, that of lactam be a_3, and the degree of polymerization be n. The activity of the x-mer is $a_2(1 - 1/n)^{x-1}/n_2$; of the y-mer, $a^2(1 - 1/n)^{y-1}/n^2$; and of the $(x + y)$-mer $a_2(1 - 1/n)^{x+y+1}/n^2$. Substituting in eqn. (1), we have :

$$K_1 = a_1n(n - 1)/a_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The mol. fraction of monomer ($x = 1$) in the polymer is $1/n^2$. Hence :

$$K_2 = a_1a_3n^2/a_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The ratio $(x + 1)$-mer/x-mer $= (n - 1)/n$. Hence :

$$K_3 = (n - 1)/na_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Eqns. (4), (5), and (6) are not independent; by combining any two, the third is obtained : $K_1 = K_2K_3$.

[14] Flory, *Chem. Rev.*, 1946, **39**, 174.
[15] Taylor, *J. Amer. Chem. Soc.*, 1947, **69**, 638.
[16] Flory, " Principles of Polymer Chemistry," Cornell Univ. Press, New York, 1953.

For the purposes of the phase rule, the system lactam–water may be regarded as a system of two components, *viz.*, water and the "unit" $-NH\cdot[CH_2]_5\cdot CO-$. A system of two components in the presence of a liquid phase and a vapour phase has two degrees of freedom, temperature and composition. If the temperature and composition of the system are defined, all other properties of the system are defined, such as the activities a_1, a_2, a_3, the proportions of unit mols. as polymer and lactam, the degree of polymerization of the polymer, the proportion of free water and of water bound as terminal groups of the polymer, and the partial pressures of water and lactam in the vapour phase.

The composition may be defined conveniently as follows:

N_1 = (mols. of water)/(mols. of water + mols. of unit)

N_2 = (mols. of unit as polymer)/(mols. of water + mols. of unit)

N_3 = (mols. of unit as lactam)/(mols. of water + mols. of unit)

$$N_1 + N_2 + N_3 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

"Mols. of water" includes both free water and water bound as terminal groups of the polymer. In the present treatment the cyclic dimers, trimers, and tetramers are included in the polymer.

Other systems could be used to define the composition. "Free water" could be used instead of total water:[3, 4, 8, 9] for this one requires to know the degree of polymerization of the polymer. Or "moles./litre" of the components, requiring a knowledge of the density.[9] "Moles./kilogramme" has also been employed.[9] None of these offers any advantage. It would certainly be convenient if methods for defining the composition could be found for which $N_1 = a_1$, $N_2 = a_2$, and $N_3 = a_3$; but none of the other possibilities does this, and in view of the complexity of the system it is impossible to derive such a system theoretically. Deviations from ideal behaviour are to be expected on the following grounds: (1) a heat of mixing arising from the interaction of water with $-CO\cdot NH-$ groups; (2) a Debye–Hückel effect, arising from the change in the concentration of $-CO_2^-$ and $-NH_2^+$ groups, and of the dielectric constant, with composition; and (3) an abnormal entropy of mixing, such as is always found in polymer–solvent systems.

From the Gibbs–Duhem equation, we have:

$$N_1\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T + N_2\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T + N_3\left(\frac{\partial \ln a_3}{\partial N_1}\right)_T = 0 \quad . \quad . \quad . \quad (8)$$

From eqn. (6), by taking logarithms and differentiating with respect to N_1, at constant temperature, and since $(\partial \ln K_3/\partial N_1)_T = 0$, we obtain:

$$\left(\frac{\partial \ln a_3}{\partial N_1}\right)_T = \left(\frac{\partial}{\partial N_1}\cdot \ln \frac{n-1}{n}\right)_T$$

Substituting in eqn. (8) gives:

$$N_1\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T + N_2\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = -N_3\left(\frac{\partial}{\partial N_1}\cdot \ln \frac{n-1}{n}\right)_T \quad . \quad . \quad (9)$$

From eqn. (4), by taking logarithms and differentiating with respect to N_1 at constant temperature, and since $(\partial \ln K_1/\partial N_1)_T = 0$, we derive:

$$\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = -\left[\frac{\partial}{\partial N_1}\cdot \ln n(n-1)\right]_T \quad . \quad . \quad . \quad (10)$$

Hence:

$$(N_1 + N_2)\left(\frac{\partial \ln a_1}{\partial N_1}\right)_T = -N_2\left[\frac{\partial}{\partial N_1}\cdot \ln n(n-1)\right]_T + N_3\left(\frac{\partial}{\partial N_1}\cdot \ln \frac{n}{n-1}\right)_T \quad (11)$$

$$(N_1 + N_2)\left(\frac{\partial \ln a_2}{\partial N_1}\right)_T = N_1\left(\frac{\partial}{\partial N_1}\cdot \ln n(n-1)\right)_T + N_3\left(\frac{\partial}{\partial N_1}\cdot \ln \frac{n}{n-1}\right)_T \quad (12)$$

From these equations it is possible to calculate $(\partial \ln a_1/\partial N_1)_T$ and $(\partial \ln a_2/\partial N_1)_T$ if N_2, N_3, and n are known over the range from $N_1 = 0$ to 1. But the equations are unsuitable for graphical integration, since as $N_1 \longrightarrow 0$, $\ln n(n-1) \longrightarrow +\infty$; and as $N_1 \longrightarrow 1$, $\ln n(n-1) \longrightarrow -\infty$, and $\ln n/(n-1) \longrightarrow +\infty$.

Let an " apparent equilibrium constant," $\bar{K}_1$, be defined by :

$$\bar{K}_1 = (N_1/N_2) \cdot n(n-1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

Then
$$\left[\frac{\partial}{\partial N_1} \cdot \ln n(n-1)\right]_T = \frac{1}{\bar{K}_1} \cdot \left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T + \frac{1}{N_2}\left(\frac{\partial N_2}{\partial N_1}\right)_T - \frac{1}{N_1} \quad . \quad . \quad (13)$$

Similarly,
$$\bar{K}_3 = (n-1)/nN_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

and
$$\left(\frac{\partial}{\partial N_1} \cdot \ln \frac{n}{n-1}\right)_T = -\frac{1}{\bar{K}_3} \cdot \left(\frac{\partial \bar{K}_3}{\partial N_1}\right) - \frac{1}{N_3} \cdot \left(\frac{\partial N_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (14)$$

Also, if $a_1 = \gamma_1 N_1$, and $a_2 = \gamma_2 N_2$, then :

$$(\partial \ln a_1/\partial N_1)_T = (\partial \ln \gamma_1/\partial N_1)_T + 1/N_1 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and
$$(\partial \ln a_2/\partial N_1)_T = (\partial \ln \gamma_2/\partial N_1)_T + \frac{1}{N_2} \cdot \left(\frac{\partial N_2}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad (16)$$

Combining eqns. (11) with (13), (14), and (15), and since, from (7), $(\partial N_3/\partial N_1)_T = -(1 + \partial N_2/\partial N_1)_T$, we find :

$$(N_1 + N_2)\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T = -\frac{N_2}{\bar{K}_1}\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T - \frac{N_3}{\bar{K}_3} \cdot \left(\frac{\partial \bar{K}_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (17)$$

Combination of eqns. (12) with (13), (14), and (15) gives :

$$(N_1 + N_2)\left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = \frac{N_1}{\bar{K}_1} \cdot \left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T - \frac{N_3}{\bar{K}_3} \cdot \left(\frac{\partial \bar{K}_3}{\partial N_1}\right)_T \quad . \quad . \quad . \quad (18)$$

Check : from eqns. (17) and (18) we have :

$$\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = -\frac{1}{\bar{K}_1} \cdot \left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (19)$$

From eqns. (4) and (4*a*), $K_1/\bar{K}_1 = \gamma_1/\gamma_2$; $\ln \gamma_1 - \ln \gamma_2 = \ln K_1 - \ln \bar{K}_1$

Hence,
$$\left(\frac{\partial \ln \gamma_1}{\partial N_1}\right)_T - \left(\frac{\partial \ln \gamma_2}{\partial N_1}\right)_T = -\frac{1}{\bar{K}_1} \cdot \left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Now $\ln \gamma_1$ and $\ln \gamma_2$ can be evaluated by graphical integration from eqns. (17) and (18), if the values of N_2, N_3, $\bar{K}_1$, and $\bar{K}_3$ are known over the whole range from $N_1 = 0$ to 1. The integration constants will depend upon the standard states selected for water and polymer.

The necessary data can be obtained from recent publications.[3,4,8-10,12,13] If W_1 is the number of moles of water per mole of lactam in the initial reaction mixture, and W_3 is the weight fraction of lactam in the mixture (polymer + lactam) at equilibrium, it is found empirically that W_3 varies linearly with W_1. We have :

At 221·5°
$$W_3 = 0{\cdot}059 + 0{\cdot}035W_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

At 253·5°,
$$W_3 = 0{\cdot}076 + 0{\cdot}042W_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

$$N_1 = W_1/(1 + W_1); \; N_2 = (1 - W_3)/(1 + W_1) \; ; \; N_3 = W_3/(1 + W_1)$$

The activity of a solvent in a polymer–solvent system can usually be evaluated, in the region of high concentration, by regarding the system as a mixture of solvent molecules and " segments " of the polymer which act as independent molecules. The activity of the solvent is then proportional to the mol. fraction as given by (mols. of solvent)/(mols. of solvent + mols. of " segments ").

Eqn. (20) and (21) may be written in the form :

$$W_2 = 0{\cdot}059(1 + W_1/1{\cdot}69) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20a)$$

$$W_2 = 0{\cdot}076(1 + W_1/1{\cdot}81) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21a)$$

From eqn. (20*a*), the addition of 1·69 mols. of water to the polymer–lactam mixture when $W_1 = 0$ will double W_2, the mols. of lactam. From eqn. (6), the activity of lactam, a_2, is constant, except in so far as $(n - 1)/n$ varies from unity. Therefore, the addition of

TABLE 1.

W_1	E	W_2	W_3	N_1	N_2	N_3	n	$\bar{R}_1$	$\bar{R}_2$
				$T = 221{\cdot}5°$.					
0	0	0·059	0·941	0	0·941	0·059	∞	(750)	16·9
0·05	0·070	0·061	0·939	0·0476	0·894	0·058	119	748	17·1
0·1	0·099	0·063	0·937	0·0909	0·852	0·057	84·1	743	17·3
0·2	0·141	0·066	0·934	0·167	0·778	0·055	58·4	720	17·9
0·4	0·204	0·073	0·927	0·286	0·662	0·052	40	672	18·8
0·6	0·259	0·080	0·920	0·375	0·575	0·050	31·3	619	19·4
0·8	0·310	0·087	0·913	0·444	0·508	0·048	25·9	564	20·0
1·0	0·360	0·094	0·906	0·500	0·453	0·047	22·1	515	20·3
1·2	0·408	0·101	0·899	0·545	0·409	0·046	19·3	473	20·6
1·4	0·453	0·108	0·892	0·583	0·372	0·045	17·3	440	20·9
1·6	0·494	0·115	0·885	0·615	0·341	0·044	15·7	416	21·3
1·8	0·532	0·122	0·878	0·643	0·314	0·0435	14·4	397	21·4
2·0	0·578	0·129	0·871	0·667	0·290	0·043	13·2	368	21·5
				$T = 253{\cdot}5°$.					
0	0	0·076	0·924	0	0·924	0·076	∞	(520)	13·2
0·05	0·083	0·078	0·922	0·0476	0·878	0·074	97·6	511	13·3
0·1	0·120	0·080	0·920	0·0909	0·836	0·073	68	495	13·5
0·2	0·172	0·084	0·916	0·167	0·763	0·070	47	473	13·9
0·4	0·243	0·093	0·907	0·286	0·648	0·066	33	466	14·6
0·6	0·306	0·101	0·899	0·375	0·562	0·063	26	434	15·2
0·8	0·355	0·110	0·890	0·444	0·495	0·061	22	414	15·7
1·0	0·403	0·118	0·882	0·500	0·441	0·059	19·2	396	16·1
1·2	0·442	0·126	0·874	0·545	0·398	0·058	17·3	386	16·4
1·4	0·480	0·135	0·865	0·583	0·361	0·056	15·8	376	16·7
1·6	0·516	0·143	0·857	0·615	0·330	0·055	14·5	365	16·9
1·8	0·546	0·152	0·848	0·643	0·303	0·054	13·6	364	17·1
2·0	0·580	0·160	0·840	0·667	0·280	0·053	12·7	354	17·4

1·69 mols. of water has doubled the total number of mols. in the system, and the mixture of polymer and lactam from 1 mol. of lactam, at equilibrium, contains 1·69 (mols. + segments). Of these, 0·059 are lactam, so that 0·94 mole of polymer contains 1·63 " segments," and the " segment weight " is 65, equal to 3·6 water molecules. From eqn. (21*a*) at 253·5°, the segment is 0·53 of a unit and the segment weight 60, equal to 3·35 water molecules. A similar calculation for the system thymol–polyaminohexanoic acid [10] gave a value of 2·3 for the ratio " segment weight "/molecular weight of diluent, constant from 200° to 275°. A polymer chain of 6 units would consist of 10 segments with respect to water; therefore, even at this low degree of polymerization one might expect interaction between polymer chains and water molecules to be independent of chain length, and the same as for higher degrees of polymerization.

In Table 1 are given experimental values for W_1, the mols. of water per mol. of lactam in the original reaction mixture; W_2, the weight fraction of lactam in the dry reaction product, and E, the milliequivalents of end groups per g. in the dry reaction product. The figures were obtained from the graphical data published by Hermans, and van Velden, and

their co-workers.[8,9] From them the following derived quantities have been calculated; W_2, the weight fraction of polymer in the dry reaction product; n, the number average degree of polymerization; the mol. fractions N_1, N_2, and N_3, as previously defined; and the apparent equilibrium constants $\bar{K}_1$ and $\bar{K}_3$. The experimental values extend only from $N_1 = 0$ to $N_1 = 0{\cdot}667$. Over this range N_2, N_3, and $\bar{K}_3$ are linear functions of N_1 at both 221·5° and 253·5°, and it will be assumed that they can be extrapolated linearly from $N_1 = 0{\cdot}667$ to $N_1 = 1{\cdot}0$. The values for N_2 and N_3 calculated from Matthes's data [13] at 220° are in agreement with this extrapolation.

$\bar{K}_1$ is a linear function of N_1 at 253·5° over the range $N_1 = 0$—0·667, and it will be assumed that it can be extrapolated linearly to $N_1 = 1{\cdot}0$. At 221·5°, $\bar{K}_1$ is not linear from $N_1 = 0$ to $N_1 = 0{\cdot}45$, but appears to be so from $N_1 = 0{\cdot}45$ to $N_1 = 0{\cdot}667$, and it will be assumed that it can be extrapolated linearly to $N_1 = 1{\cdot}0$. The plot of $\bar{K}_1$ at 221·5° and 253·5° against N_1 is shown in Fig. 1. The plot of $\bar{K}_1$ for 7-aminoheptanoic acid from

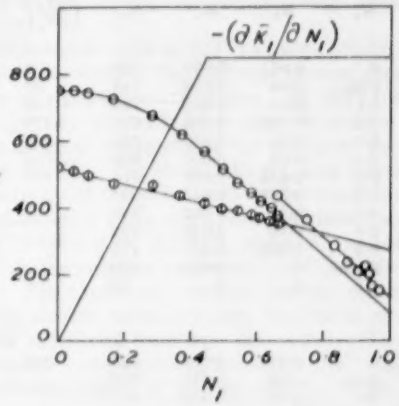


FIG. 1. *$\bar{K}_1$ for 6-aminohexanoic acid at ⊖ 221·5° and ⊕ 253·5°, and for ○ 7-aminoheptanoic acid at 220°.*

$N_1 = 0{\cdot}667$ to $N_1 = 1{\cdot}0$ at 220°, from Wiloth's data,[3] is also shown. It will be seen that this is linear, and the slope is almost the same as for $\bar{K}_1$ for 6-aminohexanoic acid, so that the linear extrapolation appears to be justified. The plots of $\bar{K}_1$ at 221·5° and 253·5° cross at $N_1 = 0{\cdot}70$. The slope of the curve for $\bar{K}_1$ at 221·5° from $N_1 = 0$ to $N_1 = 0{\cdot}45$ is determined by assuming that $(\partial \bar{K}_1/\partial N_1)_T = 0$ at $N_1 = 0$, and decreases linearly to −850 at $N_1 = 0{\cdot}45$; from then onwards it remains constant. The plot of $-(\partial \bar{K}_1/\partial N_1)_T$ is also shown on Fig. 1. The abrupt change at $N_1 = 0{\cdot}45$ is unsound mathematically, but the values obtained for $(\partial \bar{K}_1/\partial N_1)_T$ are probably sufficiently accurate. The plot of $\bar{K}_1$ in this region fits the experimental points reasonably.

From the plots of N_2, N_3, $\bar{K}_1$, and $\bar{K}_3$ against N_1, extrapolated where necessary, the values of these quantities at regular increments of N_1 were obtained. These are given in Table 2; from them the corresponding values of $(\partial \ln \gamma_1/\partial N_1)_T$ and $(\partial \ln \gamma_3/\partial N_1)_T$ were calculated. The values of $\ln \gamma_1$ and $\ln \gamma_3$ were obtained by summing the differential by the trapezoidal rule; a more accurate method is probably not justified. The magnitude of the integration constant is determined by the standard states chosen for water and polymer.

For water, the standard state is liquid water at the temperature of the reaction. Then $\ln \gamma_1 = 0$ when $N_1 = 1{\cdot}0$; and when $N_1 = x$, $\ln \gamma_1 = -\int_{N_1=x}^{N_1=1} (\partial \ln \gamma_1/\partial N_1) dN_1$.

For polymer, the standard state is polymer of infinite chain length ($N_1 = 0$), and in

equilibrium with its lactam at the reaction temperature. This convention is both mathematically convenient and experimentally sound. Polymer free from lactam would, under this convention, have a positive free energy, but above its melting point it would quickly revert to the equilibrium mixture of polymer and lactam, for which, by this convention, $\Delta F = 0$.

Since $\ln a_2 = \ln N_2 + \ln \gamma_2 = 0$ when $N_1 = 0$, $\ln \gamma_2 = -\ln N_2$ when $N_1 = 0$; when $N_1 = x$, $\ln \gamma_2 = -\ln N_2(N_1 = 0) + \int_{N_1=0}^{N_1=x} (\partial \ln \gamma_2/\partial N_1) dN_1$.

Table 2 gives the values for $\log \gamma_1$, $\log \gamma_2$, and γ_1/γ_2 from $N_1 = 0$ to $N_1 = 1{\cdot}0$, at 221·5° and at 253·5°.

The values depend on the correctness of the extrapolation of $\bar{K}_1$ from $N_1 = 0{\cdot}70$ to $N_1 = 1{\cdot}0$; the influence of $\bar{K}_2$ is relatively small. The apparent equilibrium constant for

TABLE 2.

N_1	N_2	N_3	$\bar{K}_1$	$\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T$	$\bar{K}_2$	$\left(\frac{\partial \bar{K}_2}{\partial N_1}\right)_T$	$\log \gamma_1$	$\log \gamma_2$	γ_1/γ_2	K_1
					$T = 221{\cdot}5°$.					
0	0·94	0·059	750	0	16·7	7·3	−0·205	0·0264	0·587	440
0·05	0·89	0·058	746	− 90	17·0	,,	−0·204	0·0257	0·589	439
0·1	0·84	0·057	740	−180	17·4	,,	−0·201	0·0248	0·594	440
0·2	0·745	0·055	712	−370	18·1	,,	−0·189	0·0208	0·617	439
0·3	0·65	0·052	665	−560	18·9	,,	−0·168	0·0117	0·661	439
0·4	0·55	0·050	600	−750	19·6	,,	−0·141	−0·0063	0·733	440
0·5	0·455	0·047	515	−850	20·35	,,	−0·109	−0·0373	0·847	436
0·6	0·355	0·045	432	,,	21·05	,,	−0·077	−0·0836	1·016	439
0·7	0·26	0·042	347	,,	21·8	,,	−0·047	−0·150	1·267	440
0·8	0·16	0·040	262	,,	22·6	,,	−0·022	−0·248	1·684	441
0·9	0·065	0·037	175	,,	23·3	,,	−0·004	−0·406	2·524	442
0·965	0	0·035	120	,,	23·8	,,	−0·0002	−0·570	3·71	445
1·0	0	0	90	,,	24·0	,,	0	−0·696	4·96	447
									Mean =	440
					$T = 253{\cdot}5°$.					
0	0·92	0·076	520	−245	12·7	6·7	−0·1043	0·0343	0·727	378
0·05	0·88	0·075	510	,,	13·05	,,	−0·0952	0·0331	0·744	379
0·1	0·83	0·073	497	,,	13·4	,,	−0·0863	0·0314	0·763	379
0·2	0·73	0·069	473	,,	14·05	,,	−0·0696	0·0262	0·802	379
0·3	0·63	0·066	447	,,	14·6	,,	−0·0541	0·0185	0·846	378
0·4	0·54	0·063	423	,,	15·25	,,	−0·0401	0·0080	0·895	379
0·5	0·44	0·059	398	,,	16·1	,,	−0·0279	−0·0057	0·950	378
0·6	0·345	0·056	374	,,	16·75	,,	−0·0175	−0·0229	1·013	379
0·7	0·25	0·052	350	,,	17·45	,,	−0·0093	−0·0441	1·083	379
0·8	0·15	0·049	325	,,	18·1	,,	−0·0036	−0·0701	1·165	379
0·9	0·055	0·045	300	,,	18·75	,,	−0·0007	−0·1010	1·260	378
0·955	0	0·045	287	,,	19·1	,,	−0·0002	−0·1204	1·319	379
1·0	0	0	275	,,	19·4	,,	0	−0·1373	1·373	378
									Mean =	379

eqn. 5, $\bar{K}_2 = \bar{K}_1/\bar{K}_3$, has a limiting value of 3·75 at 221·5°, and 14 at 253·5°, when $N_1 = 1$. It follows that in a dilute solution of 6-aminohexanoic acid, about 80% will be converted into lactam at 221·5°, and 93% at 253·5°. Technical data [12] show that when the polymer is heated with 64 mols. of water at 220°, 60% is converted into lactam, and the remainder is not all 6-aminohexanoic acid; some dimer and trimer are present. At 260°, with 32 mols. of water, conversion into lactam is 76%. It follows that $\bar{K}_1$ cannot be very small, in the limit; it must be at least 2—3 times $\bar{K}_3$. If $\bar{K}_1$ at 221·5° is extrapolated linearly to 50 at $N_1 = 1$, instead of 90, this will not affect the value of $\log \gamma_2$ from $N_1 = 0$ to $N_1 = 0{\cdot}7$, since the standard state for polymer is at $N_1 = 0$, and the integal is summed from $N_1 = 0$. Beyond $N_1 = 0{\cdot}7$, the deviation is considerable, owing to the increase in $1/\bar{K}_1$ in $\frac{N_2}{\bar{K}_1}\left(\frac{\partial \bar{K}_1}{\partial N_1}\right)_T$. The value of $\log \gamma_1$ is affected throughout the whole range, since the standard state for

water is $N_1 = 1$, and the integal is summed towards $N_1 = 0$. Calculation shows that $\log \gamma_1$ would be increased by about 0·01 from $N_1 = 0{\cdot}7$ to $N_1 = 0$, corresponding to an error of 28% at $N_1 = 0{\cdot}7$, but only about 5% over the range $N_1 = 0$—0·1. It seems probable that at 221·5° $\log \gamma_1$ and $\log \gamma_2$ are within 5—10% of the true values from $N_1 = 0$ to $N_1 = 0{\cdot}1$, and that the error is no greater at 253·5°.

The value of the true equilibrium constant K_1 is 440 at 221·5° and 379 at 253·5°. From these values, $\log K_1$ is given by :

$$\log K_1 = 1{\cdot}569 + 531/T \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$\Delta H = -2{\cdot}42$ kcal./mole, and $\Delta S = 7{\cdot}16$ cal./mole^{-1} degree^{-1}. These values are different from those previously calculated, which were based on data from an alkali-catalysed polymerization.[1] The reaction between a carboxyl and an amino-group (to form an amide) appears to be exothermic in the polyamide melt; the reaction between glycine molecules to form glycine peptides in the solid state is endothermic, as calculated from the heats of combustion.[17] The difference may be due to the heats of fusion. The rather low value for the entropy of the re on suggests that in the melt the carboxyl and amino-groups exist largely as uncharged groups, and not as zwitterions.

The equilibrium between steam and polyaminohexanoic acid at 293° has been studied by Meacock.[18] In his experiments a polymer in which some of the terminal groups were acetylated was held at 293° for several hours in an atmosphere of steam. At 293° the saturation pressure of steam is 76·9 atm.; the activity of steam at 1 atm., referred to liquid water as standard state, is 0·013. In one series of experiments the polymer contained 0·00836 equiv. of CO_2^- and 0·00373 equiv. of NH_3^+ per mole (113 g.), and hence 0·992 equiv. of –CO·NH–. Assuming that the activity of the polymer is unity, since the amount of free water in the system will be very small under these conditions, and inserting these values in the expression, $K_1 = (H_2O)(\text{–CO·NH–})/(CO_2^-)(NH_3^+)$, gives $K_1 = 414$ at 293°; for a second series of experiments, in which the polymer contained 0·00678 equiv. of CO_2^- and 0·00452 equiv. of NH_3^+, $K_1 = 421$. The agreement between the two series and the constancy of the end-group values during several hours, indicate that these are true equilibrium values. The value for K_1 at 293° calculated from eqn. (24) is 321. The discrepancy is probably due to lactam. In Meacock's experiments, although the total vapour pressure over the melt was 1 atm., an appreciable part of this was due to lactam, so that the partial pressure of steam was less than 1 atm. A partial pressure of lactam of 0·25 atm. would be sufficient to bring Meacock's result into agreement with that calculated from eqn. (24). At 293° the melt would contain about 10% of lactam.[19] Since the boiling point of the lactam is about 275°, and since its activity in the polymer melt will be greater than its weight fraction, a partial pressure of 0·25 atm. is quite possible.

From the data in Table 2, the temperature–composition diagram for the system can be constructed, with lines of equal lactam content, lines of equal partial pressure of water, and lines of equal degree of polymerization.

In order to plot the lines of equal lactam content on the diagram, it is necessary to have the graphs of lactam content (W_3) against water content (W_1) for several temperatures. Two such graphs are available from the experimental data,[9] at 221·5° and 253·5°, and have been employed in calculating the values in Table 2. Others were constructed in the following way. The plot of $\log W_3$ against $1/T$ is a straight line;[1,10] consequently the values of W_3 at different temperatures can be obtained from this plot, by using the values of W_3 at 221·5° and 253·5° when $W_1 = 0$. The graphs of W_3 against W_1 at these temperatures are linear, and intersect at $W_1 = -2{\cdot}43$; $W_3 = -0{\cdot}026$; and it may be assumed that all the graphs of W_3 against W_1 pass through the same point; such a relationship has been shown to hold for the system thymol–polyaminohexanoic acid.[10] From this set of graphs the value of W_1, and hence of N_1, for which W_3 has a given value at a given temperature, may be read off (Fig. 2).

The lines of equal partial pressure of water are obtained in the following way. The

[17] Wrede, *Z. phys. Chem.*, 1910, **75**, 92.
[18] Meacock, *J. Appl. Chem.*, 1954, **4**, 173.

activity of water in the system is given by $N_1 \gamma_1$; since, in general, $\log \gamma_1$ will be a linear function of $1/T$ to a first approximation, the function $(\log N_1 + \log \gamma_1)$ may be plotted as a linear function of $1/T$, for different values of N_1, by using the corresponding values of γ_1 at 221·5° and 253·5°. If the saturation pressure of water vapour at any temperature is p atm., the activity of water at that temperature when the partial pressure of water vapour is 1 atm. is $1/p$, and $\log 1/p$ will be a linear function of $1/T$. The values of $1/T$ at which $(\log N_1 + \log \gamma_1)$ intercepts $\log 1/p$ give the values of N_1 and T for which $p_{H_2O} = 1$ atm. The intercepts with $\log 2/p$, $\log 0{\cdot}5/p$, etc., give the values for which $p_{H_2O} = 2$ atm., 0·5 atm., etc. These graphs are shown in Fig. 3.

FIG. 2. *Plot of W_2 against W_1 for different temperatures.*

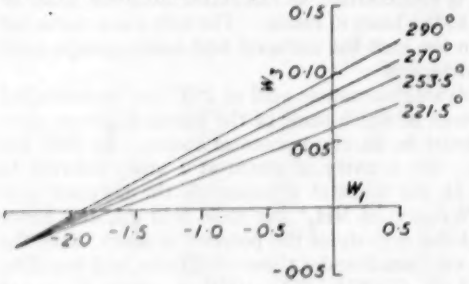
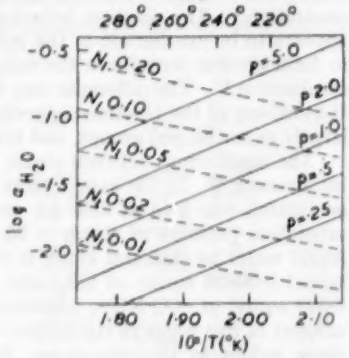


FIG. 3.



——— *Plot of* $\log p/p_{\text{sat.}}$ *against* $1/T$ *for different values of* p.
– – – – *Plot of* $(\log N_1 + \log \gamma_1)$ *against* $1/T$ *for different values of* N_1.

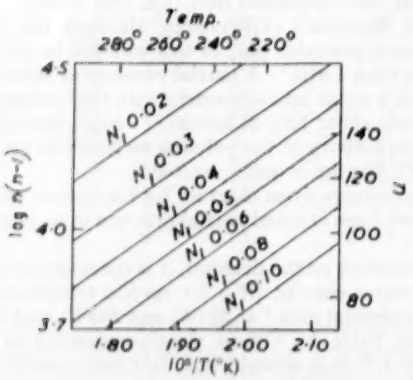
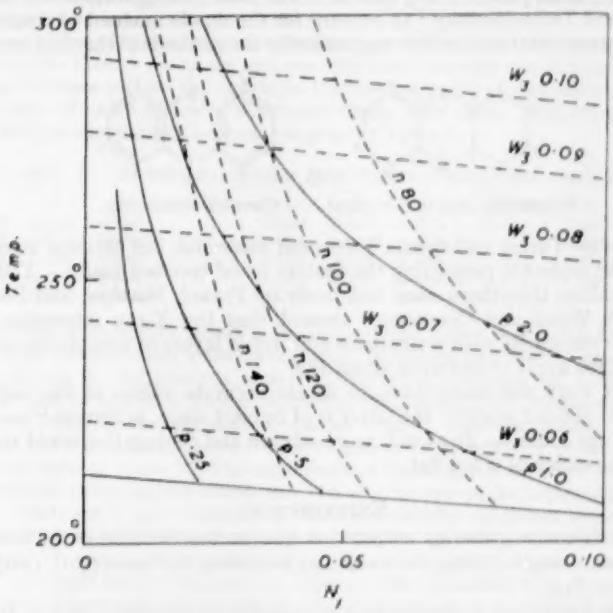


FIG. 4. *Plot of* $(\log \bar{K}_1 - \log N_1 + \log N_2)$ *against* $1/T$ *for different values of* N_1.

From eqn. (4*a*) we have: $\log \bar{K}_1 - \log N_1 + \log N_2 = \log n(n-1)$; and $\log \bar{K}_1 = \log K_1 - \log \gamma_1 + \log \gamma_2$; since these are linear functions of $1/T$, $\log \bar{K}_1$ may be so regarded. $\log N_2$ is not strictly linear with respect to $1/T$, but varies only slightly with temperature, and no great error would be introduced by assuming it to vary linearly. $(\log \bar{K}_1 - \log N_1 + \log N_2)$ was plotted against $1/T$ for different values of N_1, the values of $\bar{K}_1$ and N_2 at 221·5° and 253·5° being used. The values of $1/T$ for which the function is equal to $\log n(n-1)$ when $n = 80$, 100, 120, etc., give the values of T and N_1 for which n has these values (Fig. 4).

The composition–temperature diagram from 200° to 300°, and from $N_1 = 0$ to $N_1 = 0{\cdot}1$, is shown in Fig. 5; this is the technically important region. Spinnable polymers must lie to the left of the line $p = 1{\cdot}0$; to the right of this line the partial pressure of steam over the melt is greater than 1 atm., and bubbles will be formed at the spinneret. The higher the spinning temperature, the higher the lactam content of the melt, and the higher also the partial pressure of lactam. The minimum degree of polymerization for fibre formation is about 80; all polymers for which p_{H_2O} is less than 1 atm. have degrees of polymerization greater than this; this is in agreement with the technical observation that the polymer melt can be blanketed with steam at atmospheric pressure without causing

FIG. 5. *Temperature–composition diagram for the system: 6-hexanolactam–water.*



depolymerization. This is not possible with polyesters. The maximum degree of polymerization which is desirable is probably around 140—160; beyond this, difficulty arises during drawing. Fig. 5 shows that at 270° the polymer having a degree of polymerization of 140 has a partial pressure of water vapour of 1 atm., in addition to a significant partial pressure of lactam. In order to spin at these temperatures it is necessary to have some method of controlling the degree of polymerization other than the activity of water in the system, and this can be done by the addition of acetic or benzoic acid, which acylate some of the terminal amino-groups.

At 260°, when $N_1 = 0{\cdot}025$, the partial pressure of water is 1 atm. The degree of polymerization is about 130, so that of the total water in the system, about 0·008 mol. is bound on the terminal groups of the polymer, and 0·017 mol. is free water. This is equivalent to 0·27% by weight on the polymer. If the polymer is to be melt-spun after being washed with water to remove the free lactam, it will have to be dried to less than 0·27% of free water if bubble formation at the spinneret at 260° is to be avoided.

DEPARTMENT OF TEXTILE INDUSTRIES,
THE UNIVERSITY, LEEDS, 2.

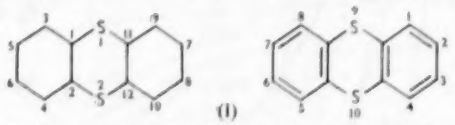
[*Received, April 25th,* 1956.]

954. *The Crystal and Molecular Structure of Thianthren.*

By H. Lynton and (in part) E. G. Cox.

A detailed *X*-ray structure analysis of thianthren, $C_{12}H_8S_2$, has been made. The molecule is folded on the S–S line, so that the two benzene rings lie in two planes at an angle of 128°. The sulphur valency angle is 100° and the C–S bond length is 1·76 ± 0·01$_8$ Å.

Thianthren (diphenylene disulphide), $C_{12}H_8S_2$ (I), has long been considered (although on circumstantial rather than direct evidence) to be an example of a folded molecule in which the folding enables the central sulphur atoms to retain their "natural" valency angles even though they form part of a ring system. The folded configuration was first suggested by Bergmann and Tschudnowsky [1] to account for the dipole moment of thianthren (about 1½ D). Attempts to substantiate this suggestion by the methods of classical stereochemistry



(I)

Numbering used in this paper. Chemical numbering.

(for a summary see Turner and Harris [2]) were not successful, but this was attributed to the flexibility of the molecule permitting the folding to be reversed easily. *X*-Ray measurements on crystalline thianthren were first made by Prasad, Shanker, and Peermohamed [3] and by Cox;[4] Wood and Crackston [5] showed that the *X*-ray intensities and optical properties were consistent with a structure built up of layers of non-planar molecules, and they estimated the angle of fold to be about 140°.

The present work was undertaken to obtain accurate values of the sulphur valency angle and the C–S bond length; the latter is of interest since, as Sutton [6] has pointed out, the sulphur atoms could use $d\pi$ as well as $p\pi$ orbitals and conjugation could therefore occur even though the molecule is not flat.

Experimental

Suitable crystals were grown by evaporation from acetone solution in the form of radiating clusters of prisms, elongated along the *b*-axis and exhibiting the forms {001}, {$\bar{1}$01}, {$\bar{2}$01}, {011}, {021}, {110}, and {$\bar{1}$11}.

The unit-cell dimensions, measured from Straumanis photographs, are $a = 14{\cdot}484 \pm 0{\cdot}002$, $b = 6{\cdot}147 \pm 0{\cdot}002$, $c = 11{\cdot}932 \pm 0{\cdot}002$ Å, and $\beta = 109°\,51{\cdot}6' \pm 1{\cdot}5'$. These results, which agree with those of Wood and Crackston, are also in accord, when suitably transformed, with the axial ratios given by Friedel and Crafts.[7] It should be noted that in Friedel and Crafts's description of the crystals, as transcribed by Groth,[8] two planes are wrongly indexed as (101) and (111); on Groth's orientation and axial ratios they should be (201) and (221) respectively.

The density determined by flotation is 1·44 g. cm.$^{-3}$ (calc. 1·44, by assuming four molecules in the unit cell). The systematic absences of (*h*0*l*) reflections for *h* odd and (0*k*0) for *k* odd indicate unambiguously that the space group is $P2_1/a - C_{2h}^5$.

An optical examination in sodium light gave the following values for the principal refractive indices and the optic axial angle, in good agreement with those of Wood and Crackston:[5] $\alpha = 1{\cdot}65$, $\beta = 1{\cdot}76$ (parallel to [*b*]), $\gamma = 1{\cdot}95$ (inclined at 69° to [*c*] in the obtuse angle β), and $2V = 82°$.

[1] Bergmann and Tschudnowsky, *Ber.*, 1932, **65**, 457.
[2] Turner and Harris, "Organic Chemistry," Longmans, Green and Co., London, 1952, pp. 783—784.
[3] Prasad, Shanker, and Peermohamed, *J. Indian Chem. Soc.*, 1937, **14**, 177.
[4] Cox, *Ann. Reports*, 1937, **34**, 189.
[5] Wood and Crackston, *Phil. Mag.*, 1941, **31**, 62.
[6] Sutton, in "Determination of Organic Structures by Physical Methods," ed. Braude and Nachod, Academic Press, Inc., New York, 1955, p. 402.
[7] Friedel and Crafts, *Ann. Chim. Phys.*, 1888, **14**, 438.
[8] Groth, "Chemische Krystallographie," 1919, Vol. V, p. 34.

X-Ray intensity measurements were made with Cu-$K\alpha$ radiation on multiple-film Weissenberg photographs about the three principal axes. The crystals employed were approximately square sections about 0·25 mm. across cut from larger crystals, and no correction for absorption effects was made ($\mu = 43$ cm.$^{-1}$). 1100 independent reflections were observed and their relative intensities were estimated visually by comparison with a standard chart.

Structure Determination

The *h*0*l* and *hk*0 intensities were put on the absolute scale by Wilson's method.[9] A Patterson *h*0*l* synthesis gave the x and y co-ordinates of the two sulphur atoms, which were then used to determine the phases of a number of terms for the first Fourier synthesis. The resultant electron-density map satisfactorily indicated the positions of the two benzene nuclei and the projection was refined by computing three further Fourier syntheses and one difference synthesis; the R factor (agreement index) was then 0·18.

The y co-ordinates of the sulphur atoms were found from the *hk*0 Patterson projection. After five successive Fourier syntheses and one difference synthesis the R factor was 0·23. In the calculation for these *h*0*l* and *hk*0 syntheses Hartree scattering factors multiplied by temperature factors with $B = 3{\cdot}8$ Å^2 and 2·5 Å^2 respectively were used. The atomic co-ordinates derived from the two-dimensional analysis are given in Table 1.

Table 1. *Atomic co-ordinates from the two-dimensional analysis.*

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
S_1	0·421	0·134	0·267	C_4	0·601	0·647	0·364	C_9	0·225	0·280	0·195
S_2	0·457	0·570	0·150	C_5	0·654	0·357	0·542	C_{10}	0·256	0·683	0·100
C_1	0·513	0·322	0·340	C_6	0·660	0·547	0·488	C_{11}	0·325	0·336	0·200
C_2	0·524	0·508	0·292	C_7	0·148	0·433	0·143	C_{12}	0·344	0·526	0·152
C_3	0·568	0·270	0·466	C_8	0·163	0·625	0·093				

A set of *hhl* structure factors, with a mean temperature factor of $B = 3{\cdot}5$ Å^2 was calculated on the University of Manchester's electronic digital computer and used to place the observed structure amplitudes on the absolute scale.[10] Differential syntheses for both observed and calculated structure factors were then computed at the atomic peak positions so as to obtain new co-ordinates corrected for termination-of-series errors. This was repeated four times, the individual scale and temperature factors found to give most satisfactory agreement in the final stage being those listed in Table 2. The significance of the scale factors introduced here may be understood from the following considerations. Ideally the two peaks, representing a particular atom in the "observed" and "calculated" electron-density syntheses respectively, should have the same heights and the same curvatures. Perfect agreement cannot be attained with the assumptions of spherically symmetrical atoms and isotropic thermal motion, but the "calculated" synthesis can be brought into approximate agreement with the "observed" by introducing two parameters for each atom, (i) a temperature factor and (ii) a scale factor. This scale factor must not be confused with the scale factor used to put the observed structure amplitudes on the absolute scale (although the two are interrelated if the absolute scaling has been brought about by making $\Sigma F_{obs.} = \Sigma F_{calc.}$); it represents a deviation from the assumption that the structure factor for zero scattering angle is equal to the atomic number, *i.e.*, it represents a loss or gain of electrons by the atom in question according as it is less or greater than unity. With the assumptions mentioned above it is doubtful if the individual scale factors have much physical significance but they can be subjected to the collective test that over a whole molecule the net loss and gain of electrons should be zero; in the present case, with the factors of Table 2 there is a net gain of about 0·4 **e**, *i.e.*, less than ½%, which is within the experimental error.

Table 2. *Individual scale and temperature factors used in final differential synthesis.*

Atom	S_1, S_2	C_1, C_2, C_{11}, C_{12}	C_3, C_4, C_9, C_{10}	C_5, C_6, C_7, C_8
Scale factor	1·05	0·94	1·02	0·99
Temperature factor (B)	3·5	3·2	3·8	4·2

If the four groups of atoms in Table 2 are put in ascending order of their temperature factors they are also in ascending order of their distances from the centre of gravity of the molecule. This effect is normally interpreted (cf., *e.g.*, acridine [11]) as evidence of rigid-body oscillation

[9] Wilson, *Nature*, 1942, **150**, 152.
[10] Wheatley, *Acta Cryst.*, 1954, **7**, 68.
[11] Phillips, *ibid.*, 1956, **9**, 237.

(libration) of the molecule, and can be partly so interpreted in this case. In addition, however, it can readily be shown that a " flapping " motion of the molecule about the S–S " hinge " would produce rather similar effects and the overall thermal motion is presumably a combination

TABLE 3.

(Densities in e Å^{-3} and curvatures in e Å^{-5}.)

Atom	ρ_o	ρ_c	ρ_o/ρ_c	$Curv_o$	$Curv_c$	$\frac{Curv_o}{Curv_c}$	Atom	ρ_o	ρ_c	ρ_o/ρ_c	$Curv_o$	$Curv_c$	$\frac{Curv_o}{Curv_c}$
S_1	25·6	26·9	0·967	214·8	229·6	0·955	C_3	6·3	6·4	0·963	52·4	54·8	0·946
S_2	26·3	26·8		225·3	231·4		C_4	7·1	7·4		61·4	65·3	
							C_8	6·0	6·4		50·3	54·4	
C_1	6·6	6·4	1·047	56·2	56·5	1·013	C_{10}	7·2	7·3		57·6	59·9	
C_2	7·1	6·7		65·0	62·1								
C_{11}	6·9	6·7		60·5	61·4		C_5	6·2	6·4	0·966	54·0	57·1	0·944
C_{12}	7·7	7·2		65·1	63·6		C_6	6·2	6·4		51·3	53·2	
							C_7	6·0	6·3		43·3	47·3	
							C_9	6·3	6·5		49·0	51·5	

TABLE 4. *Final atomic co-ordinates.*

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
S_1	0·4196	0·1330	0·2665	C_4	0·6011	0·6562	0·3662	C_9	0·2271	0·2601	0·1977
S_2	0·4553	0·5779	0·1504	C_5	0·6431	0·4092	0·5316	C_{10}	0·2591	0·6516	0·1018
C_1	0·5122	0·3159	0·3509	C_6	0·6581	0·5995	0·4808	C_{11}	0·3225	0·3155	0·2044
C_2	0·5257	0·5124	0·2981	C_7	0·1503	0·3976	0·1420	C_{12}	0·3382	0·5138	0·1513
C_3	0·5696	0·2627	0·4638	C_8	0·1638	0·5959	0·0931				

TABLE 5.

Molecular dimensions.

Bond	Length (Å)		Bond	Length (Å)	
S_1–C_1	1·778	1·759	C_3–C_5	1·419	1·391
S_1–C_{11}	1·755		C_4–C_6	1·380	
S_2–C_2	1·756		C_7–C_9	1·375	
S_2–C_{12}	1·744		C_8–C_{10}	1·391	
C_1–C_3	1·360	1·393	C_1–C_7	1·407	1·417
C_2–C_4	1·425		C_{11}–C_{12}	1·427	
C_8–C_{11}	1·399		C_6–C_8	1·369	1·382
C_{10}–C_{12}	1·386		C_9–C_4	1·394	

Angle.

C_1–S_1–C_{11}	100° 10′	C_2–S_2–C_{12}	100° 10′

of the two (together with translational motions) although in what proportions the present work is not sufficiently detailed to decide.

The last set of structure factors gave an *R* factor of 0·12 for all observed planes. The final

TABLE 6. *Perpendicular distances of atoms from the best planes through the molecule.*

Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)	Atom	Distance (Å)
S_1	+0·0008	S_1	+0·0105	C_3	−0·0145	C_9	−0·0043
S_2	−0·0165	S_2	+0·0383	C_4	+0·0078	C_{10}	−0·0435
C_1	+0·0104	C_7	+0·0409	C_5	+0·0034	C_{11}	−0·0438
C_2	+0·0188	C_8	+0·0192	C_6	−0·0101	C_{12}	−0·0172

TABLE 7. *Mean bond lengths of chemically equivalent bonds.*

Bond type	S_1–C_1	C_1–C_3	C_3–C_5	C_1–C_7	C_5–C_6	all C–C
Mean bond length (Å)	1·75$_9$	1·39$_3$	1·39$_1$	1·41$_7$	1·38$_3$	1·39$_4$

peak electron densities and mean peak curvatures are given in Table 3, and the final atomic co-ordinates and molecular dimensions in Tables 4 and 5. The complete list of observed and calculated structure factors is given in Table 8.

TABLE 8. *Observed and calculated structure factors for thianthren.*

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
0.0.2	53·5	−70·1	1.1.4	58·3	−56·5	2.2.12	7·3	− 5·9	9.3.5	5·0	− 6·3
3	73·6	−101·3	5	24·4	−21·7						
4	25·6	−20·7	6	35·6	+35·7	4.2.0	12·0	−11·0	11.3.5	9·9	−11·6
5	46·4	−44·3	7	14·9	+13·6	1	5·4	+ 5·2			
6	31·9	+24·9	11	12·3	−12·1	3	30·4	+26·2	13.3.0	6·2	+ 6·8
7	22·5	+26·9	13	9·3	+10·7	4	7·6	− 8·9			
8	20·3	+23·9				5	8·2	−10·1	0.4.0	36·9	−39·0
9	21·5	−21·2	3.1.0	19·6	+20·9	7	12·6	+12·5	2	14·8	+11·7
10	19·7	−20·9	1	23·7	+17·9				4	6·5	− 2·9
11	11·6	+13·5	2	16·0	+12·0	6.2.0	35·2	+29·9	5	15·9	+16·9
14	7·3	+ 6·5	3	39·0	+36·4	1	9·5	+ 8·5	6	14·9	+13·4
			4	59·0	−61·9	2	22·6	+21·1	7	8·3	− 7·8
2.0.0	33·8	+47·5	5	38·4	−40·0	3	8·4	− 5·7	8	17·9	−19·5
1	5·2	+ 6·4	7	29·3	+33·0	4	14·3	−11·4	9	9·6	+ 8·5
2	13·8	− 8·6	11	8·6	− 7·9	5	19·8	−19·6	10	8·3	+ 8·0
3	20·6	−21·1	12	9·4	−10·2	7	9·7	+ 9·3	11	8·2	− 7·1
4	23·3	−16·3									
5	6·8	− 2·8	5.1.0	41·0	+38·1	8.2.0	7·7	− 4·9	2.4.0	13·6	−10·3
6	5·3	− 2·7	1	18·2	−13·4	1	12·7	−10·0	1	26·0	−22·9
7	27·8	+25·3	2	14·9	−10·5	2	16·4	+14·6	2	28·1	+29·9
8	38·0	+41·2	3	15·5	+14·9	3	6·0	+ 8·0	3	27·7	+26·2
9	8·5	− 7·9	5	25·4	−31·4	4	6·9	+ 9·5	4	8·2	− 4·7
10	28·0	−28·9	7	16·9	+18·1	5	9·4	−10·9	5	29·1	−30·1
11	11·5	−10·2				6	8·3	− 9·5	6	7·9	+ 9·1
			7.1.0	20·0	+19·1	9	11·6	+ 8·8	8	9·8	−11·0
4.0.0	20·6	−20·2	1	5·8	+ 5·9				9	7·1	+ 4·7
1	64·1	+77·6	2	21·6	+18·4	10.2.0	22·6	−19·1	10	11·8	+13·0
2	27·9	+29·4	3	13·8	+14·3	2	8·6	+ 9·1			
3	10·7	− 8·7	4	10·8	+11·2	8	13·6	− 4·6	4.4.0	20·5	+20·0
4	20·5	−21·6	5	22·2	−24·7				1	41·4	−40·0
5	9·6	+ 5·0	6	6·8	−11·2	12.2.0	10·2	−10·2	2	15·4	−16·8
6	15·3	−12·8	8	12·2	+14·1				3	16·3	+13·3
7	20·1	−15·5				14.2.0	7·3	− 6·2	4	12·2	+10·2
8	13·0	+17·1	9.1.0	13·8	−13·6				5	12·0	−11·3
9	19·7	+19·1	1	18·3	+18·8	16.2.0	6·2	− 5·7	6	14·5	+17·1
11	14·2	−15·8	2	16·4	+15·8				8	10·5	−10·2
			3	21·3	+22·6	1.3.0	21·4	+18·5	9	10·9	−12·7
6.0.1	26·0	+29·3	6	21·1	−22·8	1	22·4	+19·9			
2	52·9	+65·8	7	11·7	−13·3	2	44·2	−45·5	6.4.0	20·4	+14·3
4	31·5	−32·6				3	12·4	−11·4	1	13·5	−14·3
5	19·5	−22·6	11.1.0	22·2	−23·7	4	25·6	+22·2	2	25·8	−32·1
6	18·9	+15·9	1	12·7	−11·3	5	17·7	−16·4	3	10·9	+12·9
7	15·2	−15·1	5	13·9	+15·0	6	19·1	−18·3	4	9·6	+ 8·5
9	14·0	+18·3				7	22·1	+23·2			
11	11·7	−17·3	13.1.0	15·7	−16·9	8	16·2	+14·4	8.4.0	10·8	+ 7·7
			1	15·2	−15·2				1	17·2	+16·1
8.0.0	25·9	−27·1	2	13·4	+16·7	3.3.0	5·9	+ 4·4	5	7·5	+ 7·1
1	10·3	−11·0				1	30·4	+30·7			
2	32·4	+36·7	15.1.0	10·1	− 9·9	2	7·9	− 7·8	10.4.1	7·6	+ 7·0
3	31·0	+34·4	1	10·0	−13·3	3	10·1	− 7·7	5	5·3	+ 6·0
4	37·4	−42·6				4	20·6	+20·1			
5	22·1	−24·4	0.2.1	26·8	+27·1	5	8·5	+ 8·0	12.4.0	8·1	− 8·3
6	12·6	+10·4	3	19·9	−14·5	6	11·9	− 9·2			
9	10·4	+11·3	4	22·4	−21·3	7	15·0	−13·8	1.5.0	11·0	+ 7·3
			5	22·7	−21·6				2	12·8	−14·7
10.0.0	28·0	−30·1	6	15·9	+14·7	5.3.0	17·1	−14·0	3	8·0	+ 6·6
1	40·3	−45·1	7	33·0	+32·2	1	6·9	+ 7·6	4	7·9	+ 6·0
3	53·7	+64·1	8	10·3	+ 4·7	2	10·5	+ 9·9			
6	14·8	−15·0	9	15·1	−13·3	3	16·7	−13·4	3.5.0	8·5	− 8·5
8	8·4	− 7·3	10	10·0	− 8·5	4	16·3	−15·6	1	24·6	−26·6
			11	13·2	−11·5	5	11·0	+10·6	3	5·7	+ 4·6
12.0.0	17·9	+17·3	13	10·5	+10·1	6	12·0	+10·8	4	19·6	+22·9
1	12·8	−15·1							5	8·6	+ 7·2
14.0.1	14·2	−13·4	2.2.0	22·7	+22·1	7.3.0	13·8	−12·1			
			1	39·1	+39·7	1	4·6	− 2·7	5.5.1	8·3	− 7·1
16.0.0	10·5	− 9·4	2	24·1	−25·5	2	24·2	+24·5	5	12·7	+12·8
			4	21·7	−22·0	3	5·0	+ 4·9			
1.1.0	59·8	+68·4	5	9·2	− 7·2	4	15·1	−16·9	7.5.4	12·0	−16·8
1	20·0	+19·5	7	18·5	+17·7				5	6·8	+ 7·5
2	77·9	+79·5	9	8·9	+ 6·5	9.3.0	12·4	−11·5			
3	9·0	+ 2·6	11	9·8	− 7·8	1	15·2	−18·3	9.5.1	16·6	−17·2

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$
11.5.0	13·4	+14·1
13.5.0	7·2	+ 8·0
0.6.2	12·1	− 9·5
3	19·2	+22·4
6	5·7	− 8·8
2.6.1	7·0	− 7·5
3	11·2	+10·6
4	8·2	+ 8·0
4.6.1	15·3	−14·7
4	5·8	+ 7·5
5	5·8	+ 6·1
6.6.1	7·1	− 6·7
2	9·7	−11·8
5	10·0	+13·5
10.6.0	10·8	+11·5
1.7.0	13·4	−12·3
1	8·3	− 8·0
2	11·1	+ 6·7
3	10·5	+10·9
3.7.0	6·6	− 6·5
1	17·0	−19·1
3	7·7	+ 8·2
5.7.0	6·5	+ 6·3
1	8·9	− 9·7
2	7·8	− 9·4
7.7.0	6·3	+ 7·5
$\bar{2}$.0.1	70·4	−91·3
2	58·1	−81·8
3	82·2	+110·7
4	23·3	+17·4
5	31·9	−31·4
6	39·5	+37·5
7	44·7	+46·5
8	21·6	−19·9
9	32·1	−35·6
10	22·7	−22·7
11	9·6	+14·1
13	6·2	+ 4·8
14	6·7	+10·8
$\bar{4}$.0.1	13·2	−15·2
2	67·7	−90·2
3	40·7	+40·5
4	30·9	−36·7
5	14·5	+13·7
6	38·0	+44·7
7	22·5	+23·0
8	49·0	−56·2
9	8·9	−10·8
10	15·1	+18·5
11	14·1	+11·8
14	13·8	+ 6·7
$\bar{6}$.0.1	27·7	−21·7
2	23·3	−18·1
3	48·4	−44·2
4	15·6	−16·9
5	44·3	+43·3
6	46·2	+48·0
8	39·7	−41·6
$\bar{8}$.0.9	12·7	− 6·6
12	10·3	+13·1
13	10·4	+13·1
15	8·1	−11·1
$\bar{8}$.0.1	8·5	− 5·4
2	4·2	− 2·0
3	13·7	+ 4·5
4	39·6	+34·3
5	36·5	+21·7
6	20·6	−18·1
7	45·0	−54·2
8	13·0	− 9·8
9	5·9	+10·4
10	11·1	+ 6·3
11	9·2	+ 4·3
12	11·2	+12·1
14	7·2	−10·6
15	8·5	− 5·1
$\bar{1}\bar{0}$.0.1	12·8	+10·6
2	27·5	−25·2
3	13·5	+ 8·8
4	28·1	+32·3
5	20·5	+24·4
6	13·3	−14·1
7	28·8	−31·6
8	11·5	+13·5
10	7·9	+ 1·7
11	12·3	+10·9
13	18·0	−21·6
14	8·0	−11·7
$\bar{1}\bar{2}$.0.2	16·0	−18·0
3	13·5	+14·0
4	33·4	+36·1
5	18·2	−20·5
6	24·9	−30·5
7	18·8	−15·4
8	13·1	+15·6
9	11·7	+ 8·0
11	10·0	+12·0
13	9·7	−14·3
$\bar{1}\bar{4}$.0.1	4·9	− 6·7
2	8·6	+ 5·9
3	12·4	+16·4
4	14·8	+13·9
5	21·4	−24·6
6	10·4	− 7·5
7	8·4	+12·2
$\bar{1}\bar{6}$.0.2	11·6	+15·4
3	10·9	+13·9
5	12·3	−17·1
6	9·5	− 6·2
9	8·7	+ 8·6
10	7·4	+10·5
$\bar{1}\bar{8}$.0.4	6·6	−13·9
1.1.1	42·8	−42·8
2	65·2	−65·2
3	77·3	−80·5
4	19·2	−19·7
5	34·6	+30·5
6	60·0	+61·2
7	7·1	+ 4·2
9	8·4	− 3·3
10	13·9	−15·1
11	10·4	− 9·6
1.1.13	11·9	+13·9
3.1.1	63·6	+69·9
2	70·9	−77·9
3	17·4	−19·5
5	26·5	+28·3
6	5·5	+ 5·5
8	12·6	− 7·3
9	11·5	− 9·1
10	14·5	−15·8
12	16·6	+19·3
13	7·1	+ 6·4
5.1.1	24·1	+21·7
2	52·9	−57·5
3	21·0	−19·0
4	37·9	+38·6
5	13·2	+14·0
6	5·9	− 8·6
7	14·3	+10·9
9	18·4	−18·0
10	10·3	−10·7
11	7·5	+ 8·8
12	9·3	+11·3
7.1.1	58·2	−62·0
2	43·5	−48·5
4	61·7	+63·0
5	17·7	+15·1
8	20·8	−17·3
9	28·7	−27·9
11	22·8	+25·5
12	7·3	+ 5·1
9.1.1	29·1	−32·6
2	19·4	−17·7
3	29·8	+30·5
4	17·7	+13·4
6	11·4	− 5·2
7	11·8	− 5·4
8	14·7	−15·5
9	10·7	−10·6
10	21·4	+20·7
11	20·9	+21·4
13	10·4	−10·3
11.1.2	15·0	+16·6
3	24·9	+28·4
6	9·1	− 3·1
7	19·1	−17·1
8	8·4	−10·8
9	8·4	+ 6·7
10	15·0	+15·7
13	9·6	− 7·4
13.1.2	12·7	+12·6
4	7·8	+ 2·6
6	8·4	− 5·1
7	13·7	−12·5
9	17·5	+18·9
15.1.1	9·8	+11·1
2	7·6	+ 9·0
6	7·7	−12·7
7	9·8	− 9·6
9	11·4	+11·2
17.1.1	11·3	+13·1
2.2.1	20·2	+18·3
2	35·6	−38·1
2.2.3	37·1	−36·7
4	18·4	+16·9
5	22·4	+20·6
6	15·7	+14·7
8	15·5	−11·9
9	20·3	−17·7
10	10·8	+ 9·8
$\bar{4}$.2.1	16·2	−13·4
2	19·6	−17·4
3	9·0	− 6·7
4	24·6	+21·1
7	10·6	+ 6·7
8	4·9	+ 4·8
9	16·2	−16·8
$\bar{6}$.2.1	12·3	−14·7
2	16·6	−26·4
3	29·1	−25·4
4	26·2	+22·9
6	5·4	+ 3·4
7	5·9	+ 1·6
8	6·4	− 2·5
9	17·7	−13·6
11	10·1	+10·3
$\bar{8}$.2.1	14·3	−13·7
2	9·9	− 6·5
3	11·9	− 6·5
4	29·0	+25·7
5	15·9	+12·1
8	17·8	−17·3
9	16·0	−12·0
11	17·0	+16·3
$\bar{1}\bar{0}$.2.1	9·4	−11·2
3	16·3	+15·7
4	24·4	+20·2
5	8·2	+ 4·4
6	31·7	−26·8
7	8·3	− 7·1
$\bar{1}\bar{2}$.2.2	6·5	+ 8·1
6	12·9	− 8·8
$\bar{1}\bar{4}$.2.6	15·6	−12·5
$\bar{1}\bar{6}$.2.8	10·7	+ 9·5
1.3.1	11·2	+ 9·0
2	14·5	−10·8
3	10·4	+ 6·9
4	19·1	+19·1
5	23·4	−19·7
6	9·8	− 9·0
7	29·6	+29·0
8	9·3	− 8·7
9	25·8	−26·7
$\bar{3}$.3.1	46·8	−45·2
3	9·8	+ 9·4
4	13·2	+ 9·7
5	13·3	−10·6
7	17·8	+14·6
8	6·7	− 8·2
9	7·9	−12·1
10	18·4	+20·9
12	7·5	−15·0
5.3.1	9·3	−11·1
2	28·8	+24·1

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
$\bar{5}.3.3$	10·5	+12·9	$\bar{10}.4.4$	8·0	−10·8	0.1.4	19·5	+11·6	3.2.9	9·7	+ 8·5
4	16·9	−15·4	5	16·3	−19·3	5	29·7	−33·1	10	14·8	+15·5
5	8·3	− 6·1				6	9·6	− 9·9			
6	8·0	+ 9·3	$\bar{12}.4.2$	7·7	+ 9·5	12	11·2	−12·0	5 2.0	55·0	−62·4
7	5·6	+ 2·5	3	10·0	− 8·9	14	9·9	+10·9	1	56·1	−52·1
8	5·9	− 8·8	4	6·7	− 8·1				2	44·0	+45·3
9	6·6	− 4·6	5	5·9	+ 4·9	2.1.0	20·0	+21·9	3	41·5	+41·7
12	6·5	− 8·4				1	3·5	− 3·7	6	9·4	− 9·3
13	8·4	+ 9·7	$\bar{1}.5.1$	13·1	− 7·8	3	20·9	+20·8	7	7·6	− 6·6
			2	11·4	− 9·0	4	16·0	−11·4	8	11·8	−13·5
$\bar{7}.3.1$	21·4	+19·0	3	28·4	+29·5	5	25·5	−29·0	10	13·1	+16·8
3	29·7	−26·1	4	14·3	+10·5	6	5·5	− 6·3			
4	16·1	−14·5	5	10·8	−10·5	7	6·2	+ 5·7	7.2.0	7·8	− 8·0
5	16·7	+12·9	6	15·1	−14·9	8	16·3	+18·7	1	40·3	−39·8
6	17·5	+13·9				9	12·8	−13·1	2	4·2	− 4·3
			$\bar{3}.5.1$	17·3	−17·9	10	11·8	+10·9	3	22·3	+23·8
$\bar{9}.3.1$	15·7	+15·0	2	15·3	+17·7	11	7·8	+ 9·1	4	13·4	+12·1
3	17·4	−15·5	3	27·8	+28·5	13	9·6	−12·5	5	8·5	− 9·8
4	28·5	+27·4	5	20·4	−20·7				6	11·3	−11·3
5	20·7	+19·3				4.1.0	6·7	− 5·7	7	8·7	+ 8·7
6	18·5	−17·4	$\bar{5}.5.1$	11·1	+ 8·6	3	27·7	+21·3	8	9·4	− 9·8
7	14·1	−16·1	2	12·0	+ 9·5	4	18·7	+20·1			
			3	6·5	+ 4·6	6	33·3	−37·0	9.2.1	16·5	−16·2
$\bar{11}.3.1$	8·9	+ 8·2	4	18·5	−16·2	7	6·6	− 4·1	2	20·1	−23·6
3	13·3	−11·5	5	16·0	−13·7	8	19·9	+21·0	3	10·4	+11·7
4	10·5	+11·3	7	5·2	+ 4·4				4	27·0	+25·4
6	22·8	−24·2	8	7·9	+ 1·8	6.1.0	32·5	−29·7	8	9·7	− 4·7
7	10·2	+10·1	10	6·4	+ 4·4	3	11·3	− 8·7			
8	12·3	+18·3				4	11·5	+13·6	11.2.0	11·8	+12·2
			$\bar{7}.5.1$	21·3	+22·7	5	25·7	+27·0	2	20·0	−25·3
$\bar{13}.3.4$	6·8	+ 6·1	4	14·4	−15·0	6	25·1	−26·6	3	9·6	− 8·8
5	7·9	+ 4·0							4	13·6	+14·9
9	12·8	−16·3	$\bar{9}.5.1$	12·5	+11·6	8.1.0	19·6	−19·5	5	5·6	+ 7·7
			3	7·4	− 5·4	1	13·3	+11·6			
$\bar{15}.3.1$	5·6	− 8·1				2	11·7	+ 9·5	13.2.5	9·7	+14·5
			$\bar{11}.5.1$	7·0	+ 8·4	3	15·9	−15·3			
$\bar{2}.4.1$	14·6	+ 9·7	3	10·5	−13·1	5	21·7	+21·9	0.3.1	25·1	+31·5
2	13·9	+13·6				7	12·4	−15·8	2	27·6	+30·5
3	21·2	−20·0	$\bar{2}.6.1$	13·5	−11·5	8	11·5	−12·4	3	37·5	+39·1
5	12·2	+11·4	3	20·9	+17·9				4	35·8	−34·7
6	16·0	−12·9	4	9·2	+ 9·1	10.1.0	25·4	−30·9	5	23·6	−22·7
7	12·4	−10·5	5	10·1	− 8·4	1	19·0	−19·1	6	10·1	− 9·7
9	14·6	+12·6				2	11·5	+11·3	7	25·1	+25·8
			$\bar{4}.6.1$	7·5	+ 9·4	6	10·0	+ 9·9	8	10·1	− 9·8
$\bar{4}.4.1$	23·4	+21·1	2	15·3	+22·6				9	4·8	+ 6·4
2	5·8	− 3·5	3	11·0	+ 9·6	12.1.0	15·5	+11·4	12	10·4	−10·3
3	6·5	− 5·1	5	21·2	−25·8	1	13·2	−15·2			
4	17·7	+17·8							2.3.0	5·7	+ 5·7
5	6·0	+ 5·1	$\bar{6}.6.1$	8·5	+ 7·4	14.1.0	7·6	+ 6·8	1	15·5	−14·5
6	26·8	−29·9	2	6·4	+ 5·2	1	11·1	−11·5	2	10·2	+10·7
8	16·1	+16·8							3	36·2	+38·1
9	7·4	+ 8·3	$\bar{8}.6.1$	8·3	+ 8·6	1.2.0	27·9	−28·9	4	17·0	+16·0
10	7·0	− 7·7				1	48·7	+47·2	5	36·9	−38·3
			$\bar{10}.6.3$	5·4	− 6·3	2	26·8	+22·9	6	31·0	−30·5
$\bar{6}.4.1$	26·4	+24·0				3	20·5	−16·2	8	14·1	+13·6
2	23·4	−19·4	$\bar{1}.7.5$	5·2	+ 3·3	4	17·5	−14·1	9	10·0	+10·8
3	13·2	+16·8				5	21·6	+22·2	10	8·3	+ 9·7
5	17·6	−15·9	$\bar{3}.7.1$	9·3	+ 8·0	6	11·8	−12·0			
6	18·0	−20·3	4	7·2	+10·1	7	16·8	−19·0	4.3.2	10·2	+11·9
7	19·9	+18·5	6	7·8	−10·0	8	21·9	+24·1	3	11·2	+11·2
8	18·2	+16·6				9	23·8	+27·0	4	24·3	+23·8
9	8·8	− 9·3	$\bar{5}.7.1$	9·3	+ 9·9	10	10·8	− 9·3	5	16·7	−18·1
0	7·3	− 8·5	4	4·9	+ 4·5	11	15·3	−16·1	6	18·2	−18·0
			5	8·2	−10·0	12	8·9	− 7·8	8	12·6	+13·4
$\bar{8}.4.1$	7·8	− 9·8	6	8·0	− 9·5						
2	24·8	−24·8				3.2.0	41·5	−47·1	6.3.0	10·6	−10·1
3	11·6	+11·6	$\bar{7}.7.5$	7·1	− 8·2	1	9·8	+ 8·2	4	26·6	+27·1
4	7·9	+ 8·5				2	70·0	+74·0	5	10·9	+12·2
5	11·2	−13·5	0.1.1	44·2	−49·1	4	30·9	−27·5	6	14·2	−14·1
			2	24·7	+26·5	6	10·5	+ 5·2	7	14·7	−15·7
$\bar{10}.4.2$	17·9	+16·6	3	64·3	+74·1	7	26·6	−30·1			

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
8.3.0	28·3	−30·9	6.5.0	9·5	− 9·5	$\bar{5}$.1.2	15·7	+14·3	7.2.13	8·8	− 9·5
1	10·4	−10·7	1	9·0	− 8·7	10	28·7	+31·5	14	4·8	− 9·1
4	10·1	+12·6	2	6·9	+ 6·7	11	12·7	−10·7			
5	5·1	+ 6·8	3	23·8	+24·9				$\bar{5}$.2.1	7·2	+ 4·3
			5	10·5	−10·4	$\bar{10}$.1.2	33·4	+37·1	2	10·4	−11·1
10.3.0	16·7	−16·0				4	7·9	− 7·8	3	15·3	+12·7
1	11·3	−11·9	8.5.0	9·6	+ 5·9	6	10·1	− 5·0	4	19·7	+21·0
5	8·6	+10·6	1	18·2	−19·7	9	9·7	+10·7	5	25·5	−22·9
						11	12·3	−12·7	6	40·1	−38·2
12.3.1	8·5	−10·7	10.5.0	9·8	+ 9·5	13	10·8	+13·7	7	27·0	+22·7
									8	26·4	+26·5
14.3.0	11·0	+13·0	1.6.0	10·8	+ 5·7	$\bar{12}$.1.1	19·2	+20·3	9	9·7	+ 5·5
			1	12·0	− 8·3	3	22·9	−26·7	11	7·4	− 3·9
1.4.0	12·5	−11·0	3	13·1	+10·3	4	9·3	− 7·5	12	10·5	− 7·5
1	15·8	+18·1	5	10·5	− 9·8	8	9·7	+10·1			
2	20·6	+22·7				9	12·3	+15·1	$\bar{11}$.2.1	10·4	+ 7·7
3	19·8	+17·2	3.6.0	9·1	+ 4·6	12	8·8	− 5·3	2	15·9	+13·4
4	9·5	−11·5	2	12·0	− 8·9				3	26·1	+26·7
5	28·0	−28·5	3	5·7	+ 5·4	$\bar{14}$.1.1	10·1	+11·6	4	13·5	−11·1
6	14·2	−15·2	4	9·4	− 8·3	4	7·5	+ 8·2	5	29·2	−33·4
7	13·1	+14·3				5	10·7	− 7·7	6	28·7	−22·8
8	8·6	+ 9·0	5.6.0	8·4	+ 6·1	6	9·5	−12·2	7	22·4	+20·3
9	8·1	+ 9·6	1	10·7	+ 8·5	8	11·2	+11·5	12	7·8	−10·7
			2	6·8	− 6·9	10	9·2	−10·9			
3.4.0	10·1	−13·7	3	5·8	− 4·9				$\bar{13}$.2.1	7·3	− 9·3
3	18·6	+19·5				$\bar{16}$.1.1	5·9	+ 5·7	2	7·4	+ 8·7
4	23·7	+24·5	7.6.1	7·1	+ 5·7	2	10·1	−10·9	5	14·3	−15·1
5	13·9	−14·6	5	6·3	+ 8·2				6	19·0	+17·5
6	9·8	−10·9				$\bar{1}$.2.1	84·1	−91·0	11	9·1	− 8·3
			9.6.0	10·6	− 7·9	2	13·1	−14·5	12	7·1	−11·8
5.4.0	5·2	− 4·8				3	12·6	+14·2			
1	6·8	+ 4·2	2.7.5	8·2	+ 9·9	4	15·9	+12·8	$\bar{15}$.2.1	8·3	+ 9·0
3	9·2	+11·6				5	31·1	+28·6	2	7·4	+ 9·1
4	9·7	+11·4	$\bar{2}$.1.1	5·5	− 6·5	6	60·6	+56·6	3	7·5	− 6·4
5	8·4	− 9·0	2	66·1	−80·9	7	8·3	− 8·3	4	15·0	−17·6
6	7·5	− 8·8	3	63·8	+59·5	8	37·4	−38·2	5	7·6	− 8·0
			4	65·1	+65·1	9	23·9	−24·0	6	10·6	+12·0
7.4.0	20·3	−17·5	5	25·5	+25·9	10	15·8	+18·4	7	7·3	+ 6·9
1	12·2	−12·0	6	47·0	−48·7						
3	13·5	+16·1	7	30·6	−25·7	$\bar{3}$.2.1	15·5	−12·3	$\bar{17}$.2.1	9·8	+12·4
4	9·3	+ 9·6	8	9·2	− 2·0	2	3·1	+ 6·7	3	7·2	−11·9
			11	10·2	+10·3	3	28·5	+28·5	4	7·6	− 8·9
9.4.1	11·9	−14·1	12	9·9	+11·0	4	35·5	−34·9			
4	9·9	+ 9·0				5	13·1	+15·4	$\bar{2}$.3.1	23·8	−23·8
5	5·3	+ 7·5	$\bar{4}$.1.2	70·2	−77·2	7	24·1	−25·1	2	12·7	−12·5
			3	50·5	+49·7	8	21·0	−24·0	3	7·9	+ 5·1
15.4.0	12·0	+ 8·0	4	12·9	+12·7	9	29·5	+31·7	4	42·0	+41·7
			5	10·9	−12·8	10	14·9	+15·4	5	19·2	+17·5
0.5.1	25·6	+21·8	7	23·3	+23·9				6	14·0	−11·0
2	6·7	+ 6·9	8	11·2	− 9·0	$\bar{5}$.2.1	26·0	+22·1	7	24·9	−23·8
3	20·9	−16·3	9	9·2	−12·1	2	15·5	+ 9·0	8	14·3	−11·6
6	13·1	−12·3	11	12·2	+14·1	3	11·5	+ 9·1	9	14·1	−14·1
8	17·2	+17·1	13	9·0	−12·0	4	28·2	+25·8	11	21·1	+21·1
9	8·6	+ 8·3				5	19·1	+23·4	12	11·5	+11·9
10	3·0	− 3·2	$\bar{6}$.1.1	11·9	−13·3	6	12·7	− 9·9			
11	6·8	− 7·8	2	10·9	+ 9·0	7	37·3	−41·9	$\bar{4}$.3.1	49·2	−51·6
			3	34·1	+37·3	8	16·9	−17·1	2	26·3	−25·2
2.5.0	29·1	−29·4	4	29·4	+24·1	9	22·6	+26·1	3	37·1	+37·8
1	25·5	+23·4	5	50·6	−52·1	10	5·3	+ 3·3	4	36·2	+34·9
2	22·6	+23·7	6	15·7	+12·5	12	5·0	+ 9·3	5	15·4	+11·8
4	7·9	− 3·7	8	11·1	−12·0				6	20·6	−19·7
7	11·0	− 9·1	10	22·3	+22·9	7.2.1	27·5	+25·6	8	14·8	−14·8
			13	9·4	− 9·3	3	17·5	−15·6	11	14·8	+17·1
4.5.0	23·7	−21·9				4	61·9	+58·1	12	4·5	− 6·1
3	6·5	+8·3	$\bar{8}$.1.1	9·8	− 6·3	6	22·8	−25·2			
4	5·3	− 2·8	2	24·1	+27·6	7	33·6	−30·0	$\bar{5}$.3.1	32·2	−30·7
5	6·2	− 1·7	3	8·6	− 3·7	8	11·5	+12·6	2	15·7	+14·1
6	6·4	+ 5·3	4	12·7	+ 6·5	9	9·2	+ 9·1	3	28·7	+25·7
8	6·0	− 6·5	5	24·7	−24·1	10	11·9	+ 5·3	4	9·8	+ 9·3
9	6·8	+ 8·6	7	17·2	−14·4	11	6·4	− 5·1	5	20·6	−18·9
			8	10·1	−12·9	12	6·1	+11·4	6	9·2	− 5·1

TABLE 8. (*Continued.*)

hkl	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$	*hkl*	$F_{obs.}$	$F_{calc.}$
$\bar{6}$ 3.7	6·6	− 5·9	$\bar{1}$ 4.2	11·6	−13·0	$\bar{1}$1 4.2	6·3	+ 6·5	$\bar{1}$2 5.5	9·2	− 9·7
8	7·0	− 7·6	4	21·7	+21·8	3	9·2	+7·1			
9	7·0	+ 6·0	5	11·9	+12·5	4	6·0	− 6·8	1 6.1	16·4	+12·2
10	18·1	+19·3	7	11·0	−11·8	5	8·7	− 6·5	2	17·1	−14·3
11	7·1	+ 8·7	9	10·8	−10·2				3	8·6	− 5·5
12	10·8	−11·3	12	9·0	+ 8·9	13 4.2	9·9	+ 9·5	4	10·5	+ 8·9
13	9·0	−10·1				5	8·3	− 8·3	5	8·6	+ 6·7
			$\bar{3}$ 4.1	24·5	−21·7				6	9·7	− 9·4
$\bar{8}$ 3.1	5·9	− 6·4	2	7·5	− 7·7	15 4.3	7·5	− 6·5			
2	35·9	+36·9	3	5·8	+ 5·4				$\bar{3}$ 6.2	12·1	−12·9
3	34·3	+35·6	4	15·7	+13·3	$\bar{2}$ 5.1	20·6	−18·6	3	6·5	+ 7·8
4	7·3	− 8·4	5	18·0	+17·6	2	5·8	+ 2·1	4	15·7	+16·0
5	21·5	−22·1	8	10·0	−10·7	3	8·2	+10·3	5	6·2	− 5·5
6	21·4	−17·3	11	7·8	+10·6	4	10·7	− 7·3	6	6·4	− 7·5
7	12·1	−12·8				5	6·5	+ 6·7	7	5·0	+ 4·0
9	15·3	+16·3	$\bar{5}$ 4.1	26·5	−25·9	6	12·0	+ 7·6			
10	18·6	+19·4	2	8·8	+ 8·9	8	14·1	−13·7	$\bar{5}$ 6.1	11·6	− 9·1
			3	22·0	+21·3	10	8·8	+ 9·1	2	5·1	− 4·7
16 3.1	18·2	+18·3	4	14·9	+14·1				3	11·2	+8·7
2	12·8	+13·2	6	20·0	−21·4	$\bar{4}$ 5.2	15·6	+14·6	5	11·3	−11·4
3	12·5	+11·3	7	16·8	−16·7	3	5·8	− 3·7	7	8·0	+ 9·0
4	19·0	−16·9	8	6·6	− 5·9	5	19·0	+20·1			
5	11·9	+11·1	9	6·5	+ 4·6	7	16·1	−17·2	$\bar{7}$ 6.1	9·4	− 8·1
6	8·0	− 9·8	10	12·5	+12·5	8	11·1	−11·3	2	4·8	+ 3·7
9	14·9	+16·4	11	9·5	+11·3				3	10·9	+10·1
						$\bar{6}$ 5.4	10·7	+ 8·5	6	6·8	+ 5·2
$\bar{1}$2 3.1	15·0	+16·9	$\bar{7}$ 4.1	26·7	−24·1	5	11·2	+ 8·2			
2	9·8	+ 9·8	2	18·8	+16·9	6	12·0	−12·4	11 6.3	7·0	− 9·2
3	6·2	− 7·7	3	26·7	+24·9	7	14·8	−15·9			
4	14·2	−14·1	4	5·6	+ 7·0	8	11·7	+13·5	$\bar{2}$ 7.5	4·0	− 3·2
5	12·0	−10·2	6	8·3	− 4·9	9	4·8	+ 7·1			
8	21·6	+23·2	7	13·4	−12·5				$\bar{4}$ 7.5	3·9	− 7·9
						$\bar{8}$ 5.3	7·0	+ 8·7			
$\bar{1}$4 3.1	11·1	+11·8	$\bar{5}$ 4.1	10·2	+10·4	4	12·6	+12·1	$\bar{8}$ 7.1	7·9	+ 7·7
3	9·5	− 8·5	2	13·8	+14·7				2	3·6	− 4·2
5	9·9	−10·9	3	11·7	+12·9	16 5.3	10·3	+ 8·6	3	6·2	− 4·6
8	12·8	+15·1	4	16·3	−16·3	5	16·2	−17·9	5	5·5	+ 5·6
1 4.1	28·6	−26·0	11 4.1	6·9	+ 7·9	12 5.3	6·6	+ 6·9			

DISCUSSION

The Shape and Arrangement of the Molecules.—All the atoms of the thianthren molecule lie very nearly in two planes which intersect in the sulphur atoms at an angle of 128°. Table 6 gives the perpendicular distances of the atoms from the best planes through the two halves of the molecule.

The arrangement of the molecules (see Figure) is essentially the same as that proposed by Wood and Crackston [5] for thianthren and by Wood and Williams [12] for selenanthren. The S_1–S_2 axis of the molecule is inclined to the *b*-axis at an angle of 31° and its projection on (010) makes an angle of 20° with *c* in the acute angle β. The longest direction of the molecule, at 90° to the S_1–S_2 axis, is roughly parallel to [101] and coincides approximately with the vibration direction of the slowest ray (γ) and of minimum susceptibility indicated by magnetic measurements.[13] Molecules related by a centre of symmetry interleave thus ⟋⟍⟋ with the planes of the overlapping benzene rings 3·53 Å apart, and the structure can thus be regarded as made of puckered layers parallel to the (10$\bar{1}$) planes.

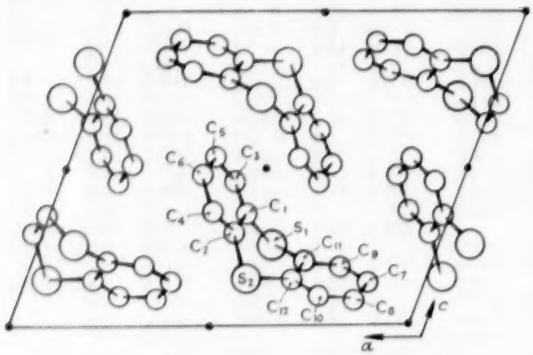
The closest-approach distances between adjacent molecules are S–C 3·92 Å, S–S 3·78 Å, and C–C 3·47 Å.

Accuracy of the Results.—A statistical calculation of the effects of random errors in the analysis was made by Cruickshank's method [14] and the mean standard deviations of the

[12] Wood and Williams, *Nature*, 1942, **150**, 321.
[13] Banerjee, *Z. Krist.*, 1939, **100**, 316.
[14] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

bond lengths found to be (range of individual values in parentheses): S–C, 0·008 (0·0071—0·0088) Å; C–C, 0·012 (0·0107—0·0147) Å. The standard deviation of the ∠CSC bond angles was 0·5° and of the electron density 0·16 e.Å^{-3}.

If the lengths of chemically equivalent bonds in the molecule are compared on the basis of these standard deviations significant differences appear, but it seems unlikely that these can be entirely real, *i.e.*, distortions due to intermolecular forces in the crystal (but see Wheatley [15]), and it is much more probable that they are systematic errors due to (*a*) the omission of hydrogen atoms from the calculations and (*b*) the assumption of isotropic thermal motion of the atoms. The scale factors and isotropic temperature factors of Table 2 were introduced in an attempt to bring the ratios of observed and calculated electron densities and mean peak curvatures to unity, but as Table 3 shows this was only



Thianthren: the structure projected on (010).

moderately successful and considerable improvement could probably be made by the use of anisotropic temperature factors. Independent justification for such factors can be found in the chemical evidence referred to in the introduction, suggesting that the thianthren molecule may be flexible about the line of fold; in the crystal the thermal motion of the molecule may be considerably greater in the directions normal to the planes of the benzene nuclei than in other directions. Further refinement, account being taken of these systematic factors, would be necessary to determine the molecular dimensions with greater precision, but it is doubtful whether the importance of thianthren justifies this. Accordingly we take as the best values of the bond lengths the means of the figures for the various groups of chemically equivalent bonds shown in Table 7. It is difficult to estimate the effect of the systematic errors on the accuracy but experience with similar cases suggests that it would be appropriate to take the " standard deviations " of the figures in Table 7 as approximately double those due to random errors, say $0{\cdot}01_8$ Å for C–S and $0{\cdot}02_5$ Å for C–C.

The C–S–C bond angle of 100° is the same as that found in 1 : 4-dithiadiene [16] and agrees fairly well with C–S–C angles in various non-cyclic compounds, so that the experimental evidence supports the view that folding of the molecule enables the sulphur atom to retain its " natural " valency angle. Possibly this tendency is assisted by a certain amount of $d\pi$ conjugation as suggested by Sutton [6] since the C–S bond length (which is in good agreement with other values in aromatic substances, *e.g.*, 1·76 ± 0·02 Å in dibenzenesulphonyl sulphide [17]) appears to be significantly less than the usually accepted single-bond value of about 1·81 Å. The mean length of the C–C bonds in the two benzene nuclei is in good agreement with recent values for benzene itself.[18]

We are indebted to Dr. G. M. Bennett, F.R.S., for the thianthren. We acknowledge gratefully a maintenance award to one of us (H. L.), and financial support from the Department of

[15] Wheatley, *Acta. Cryst.*, 1953, **6**, 369.
[16] Howell, Curtis, and Lipscomb, *ibid.*, 1954, **7**, 498.
[17] Mathieson and Robertson, *J.*, 1949, 724.
[18] Stoicheff, *Canad. J. Phys.*, 1954, **32**, 339; Cox, Cruickshank, and Smith, *Nature*, 1955, **175**, 766.

Scientific and Industrial Research, the loan of apparatus from the Royal Society and Messrs. Imperial Chemical Industries Limited. The calculations on the Manchester University electronic computer were carried out by Dr. D. W. J. Cruickshank and Miss D. E. Pilling, whom we thank.

Department of Inorganic and Structural Chemistry,
The University, Leeds, 2. [*Received, May 28th,* 1956.]

955. d-*Orbital Contraction in Chemical Bonding.*

By D. P. Craig and E. A. Magnusson.

In molecules such as phosphorus pentachloride and sulphur hexafluoride the bonds can be described as covalent *dsp* hybrids, but a study of overlap integrals shows that the *d* orbitals of phosphorus and sulphur in the free atoms are too weakly bound and diffuse to contribute to the bond energy. A type of polarization is proposed in which such diffuse orbitals are contracted, bringing the electrons closer to the atoms or groups to which bonds are to be formed and so adapting them better to bonding. Charge transfer from the central atom into orbitals of the outer atoms is not considered, but the tendency for charge to accumulate there is manifest in the contraction of the central atom's orbitals. Some features of the contraction are examined in a model in which the potential field of outer atoms is replaced by a Coulomb field and the energy of the electron minimized with respect to the exponent in a Slater orbital. Applied to real molecules the results from the model suggest that contraction is enough to allow substantial participation by *d* orbitals in covalent bonding of this type.

In an analysis of the conditions under which bonds might be formed using *d* and *f* atomic orbitals, a problem which has to be solved if the covalent-bond model is to be retained at all is that in a number of theoretically important cases the orbitals are apparently much too weakly bound and diffuse to participate appreciably in bonding. We shall find, for example, that without some hypothesis of modification of the orbital sizes, the suggestion that sulphur hexafluoride SF_6 is held by d^2sp^3 covalent bonds using sulphur $3d$ orbitals is untenable. It has been suggested that the difficulty arises from the use of free-atom parameters for the *d* orbitals, and that modifications occur in molecule formation by polarisation due to the attached groups. Craig, Maccoll, Nyholm, Orgel, and Sutton [1] noted that *d* orbitals which were as weakly bound as the free-atom data required (according, *e.g.*, to Slater's rules which, even if not really precise in such cases, are certainly correct in the qualitative sense of giving very low ionization potentials) would be strongly polarized by electronegative ligands through the partial withdrawal of charge from the weakly bound orbitals of the central atom and a tightening of the remaining charge to a size compatible with binding. In a general way this certainly describes what happens, but in detail it is not easily combined with a discussion of covalent-bond strengths in terms of overlap integrals; this is easily seen, for, if the withdrawal of charge proceeds to the point where $S^{2+}(F_6)^{2-}$ describes the electronic situation only four of the bonds are covalent and they are based on the $3s3p^3$ configuration of S^{2+}. The *d* overlap integral then has no bearing on the case, and its importance is reduced progressively as this limit is approached. For this reason we prefer to retain a description of the polarization which allows the bonding to be described without charge transfer. This does not imply the unrealistic limitation that the bonds divide their charge equally between the bound centres: on the contrary, the region of overlapping charge is much nearer to the more electronegative centre, as commonsense requires. It is only that, as detailed more fully elsewhere,[1] we regard the asymmetry of the electron charge as homopolar rather than heteropolar in origin. The bonds may thus be polar but not ionic. In a complex system it is almost meaningless to discuss which of the homopolar and heteropolar descriptions is "right;" they have to be looked upon as different approximations to the same electron distribution, both having

[1] Craig, Maccoll, Nyholm, Orgel, and Sutton, *J.*, 1954, 332.

useful features. In this paper we shall develop a description of the polarization of weakly bound orbitals by electronegative ligands which is compatible with the covalent-bond model. Our discussion, which follows an outline given earlier,[2,3] will be found to agree in most important consequences with that given by Craig *et al.*[1] in qualitative terms, but its underlying mechanism is somewhat different. The discussion begins with a description of the overlap criterion for bond strength, continues with a treatment of polarization in terms of the contraction of the loosely bound orbitals, and the detailed application of this to a series of highly idealized model situations, and ends by noting briefly the relevance of the idea of orbital contraction to the understanding of conditions in molecules.

The covalent-bond model is a *model* in the sense that it idealizes a complex situation to something very simple in the expectation that calculations based upon it will enable some of the properties of the actual system to be interpreted. In particular, each bond between the central atom A and a ligand atom B is idealized by the supposition that it is formed from appropriately directed and simply constituted atomic orbitals ϕ_A and ϕ_B. Our purpose is to examine within this framework the conditions under which the orbital ϕ_A, which is in general a linear combination of natural atomic orbitals, is strengthened by the hybridization of *d* orbitals with *s* and *p*. As an index of bond strength we use the *overlap criterion*, *i.e.*, we assume that a value of the overlap integral (1) of about 0·1 or greater is necessary for significantly strong covalent binding.[1]

$$S = \int \phi_A(v)\, \phi_B(v)\, d\tau_v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For equivalent octahedral bonds the orbital ϕ_A is determined by symmetry in its composition from *s*, *p*, and *d* orbitals, and the overlap integral S_σ may be written as the sum (2) of contributions by the overlap integrals S_d, S_s, and S_p of the *d*, *s*, and *p* orbitals at the centre atom A with the orbital at B:

$$S_\sigma = (1/\sqrt{3})S_d + (1/\sqrt{6})S_s + (1/\sqrt{2})S_p \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Large values of S_σ are associated with strong bonds, and this requires large values for the primitive overlaps S_d, etc., in (2). Moreover, whether *d* orbitals are to be used or not depends, amongst other factors, on whether their inclusion in the hybrid bond orbital ϕ_A strengthens the bond appreciably; that is, in terms of the overlap approximation, upon whether S_d in (2) is comparable to S_s and S_p. In the specific case of sulphur hexafluoride the sulphur atom is taken to be in the valence-state configuration $3s3p^33d^2$. S_s and S_p are in the range 0·2—0·3. The two 3*d* electrons are well screened from the nucleus by the inner electrons, and S_d on account of this efficient screening and consequent diffuseness of the 3*d* orbitals is nearly zero.[1] Under these conditions we should not expect *d* hybridization to occur for the following reason. In the covalent-bond model promotion of two electrons into 3*d* orbitals occurs if the bond energy of six bonds minus the promotion energy gives a favourable energy balance compared with mechanisms of bonding not requiring promotion. If the *d* orbitals contribute nothing to the bond energy all that happens is that the bond-forming ability of the available *s* and *p* orbitals is spread over a larger number of bonds, and the potential gain in *total* bond energy will be small. It therefore seems essential to the idea of *d*-hybridization that the *d* character in the orbitals is appreciably bond-strengthening, a condition which is not satisfied by the diffuse orbitals of the free atom. It becomes necessary to allow for polarization of the *d* orbitals, and this allows their participation to be understood, as will be shown.

Orbital Contraction.—We construct a simple model to represent *d* electrons in an octahedral molecule and postpone the consideration of actual examples. A single *d* electron will be supposed to move in the field of a nucleus of charge Z_e; and upon this hydrogen-like atomic system a perturbation will be superposed consisting of six positive *

* The reason for choosing positive charges is that the field of an atom capable of forming a covalent bond is electron-attracting. The familiar theory of the effect of crystalline fields on 3*d* electrons in transition metals normally involves negative charges, because the field sources are either negative ions or electron pairs in formed bonds.

[1] Craig, *Rev. Pure Appl. Chem.*, 1954, **4**, 4.
[2] Craig and Magnusson, *J. Chem. Phys.*, 1956, **25**, 383.

charges of magnitude Z_s in a regular octahedral array of radius σ atomic units. Because the model is to be used to simulate conditions in covalent bonds no provision is made for migration of the electron into orbitals at the perturbing centres. This would be another plausible method of allowing for the movement of the electron towards the positive charges; but in the present model the electron concentrates near the perturbing charge only as the changing size of the central orbit allows: the electron is, in other words, confined to an orbital based at the central nucleus. For $Z_s = 0$ the eigenfunctions and energy levels are, of course, those of the hydrogen-like atom of charge Z_a; otherwise the charges distort the orbital, expanding it if the orbital is small compared with the radius σ and contracting if it is large. Roughly we may expect that contraction will occur if the radial maximum of the orbital is greater than σ. As will be shown this conditions holds for the *d* orbitals whose usefulness for covalent bonding is at issue. The potential of the outlying charges may be expanded as a sum in the usual $1/r$ series,[4] which reduces to the following expressions for a regular octahedral field:

$$V_{r<\sigma} = -6Z_s/\sigma - (7/2)(Z_s/\sigma)(r^4/\sigma^4)\left\{\sqrt{(2/9)}\Theta_4{}^0 + (5/8)\sin^4\theta\cos 4\varphi\right\}\ldots$$

$$V_{r>\sigma} = -6Z_s/r - (7/2)(Z_s/r)(\sigma^4/r^4)\left\{\sqrt{(2/9)}\Theta_4{}^0 + (5/8)\sin^4\theta\cos 4\varphi\right\}\ldots \quad (3)$$

where $\Theta_4{}^0$ is the normalized Legendre polynomial.

The first terms in each expression have a particularly simple interpretation. They measure the potential of a charge $-6Z_s$ spread uniformly over a spherical shell of radius σ. Inside the sphere the potential is uniform and equal to $-6Z_s/\sigma$, and outside it is that of a charge $-6Z_s$ placed at the centre of the sphere. An orbital of the unperturbed atom which lies largely inside the sphere is unaffected in form by the perturbation, but its binding energy is increased by $6Z_s/\sigma$ atomic units, corresponding to the extra energy required to ionize the electron through the charged surface. Alternatively, if the energy zero is moved down by $-6Z_s/\sigma$ in the presence of the perturbation, orbitals of this type are entirely unaffected by the first term in the potential (3). On the other hand an orbital of the unperturbed system which projects significantly beyond the radius σ is specifically perturbed by the additional attractive potential $-6Z_s/r$ acting outside the sphere. This tends to draw charge inside, until a balance is reached between the increased kinetic energy of the contracted orbital and its reduced potential energy. The effect is thus a movement of charge into the sphere, giving a more compact orbital and therefore enhanced bonding power. An orbital of this projecting type also has its binding energy increased by the perturbation, but by an amount which is less than that for an orbital wholly within the sphere. This effect, which we shall study separately before dealing with following terms in the expansion (3), might be described theoretically in several different ways. The perturbed wave function could be expanded in a series of unperturbed hydrogen-like atomic wave functions for a central nuclear charge Z_a; this expansion would converge slowly except for very small perturbing charges Z_s. A quicker convergence would be obtained with a set of atomic functions for an increased charge $Z_a + \delta$, and it would be possible to choose δ, for a given Z_s, to give optimum convergence behaviour. Elaborate calculations however are not justified; we shall show, for example, that interconfiguration mixing is small (*i.e.*, participation by orbitals of principal quantum number greater than the original), and it is adequate to take a single Slater atomic wave function of radial factor (4) and to minimize its energy with respect to the exponent α. Z_a, Z_s, and σ appear as parameters.

$$\phi_n = (2\alpha)^{n+\frac{1}{2}} r^{n-1} e^{-\alpha r/\sigma}\Big/\left\{(2n)!\ n^{2n+1}\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

For diffuse orbitals in the presence of the perturbation $\alpha > Z_a$, and since Slater radial functions have their maxima at $r_m = n^2/\alpha$, the increase in α over Z_a corresponds to a contraction of the orbital.

[4] Eyring, Walter, and Kimball, "Quantum Chemistry," Wiley, New York, 1944, p. 369.

The perturbation energy due to the first term in (3) is given by the expression (5) :

$$(\phi_n|V^0|\phi_n) = -(6Z_s/\sigma)\int_0^\sigma \phi_n^2\, r^2\, \mathrm{d}r - 6Z_s\int_\sigma^\infty \phi_n^2 r\, \mathrm{d}r \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This may be evaluated from tables.[5] We have, for $n = 3$

$$(\phi_3|V^0|\phi_3) = -(6Z_s/\sigma)(2\alpha\sigma/3)^7\,(1/6\,!)\left\{6\,!\,3^7/(2\alpha\sigma)^7 - A_6(2\alpha\sigma/3) + A_5(2\alpha\sigma/3)\right\} . \quad (6)$$

where $$A_n(\omega) = \int_1^\infty r^n\, \mathrm{e}^{-\omega r}\, \mathrm{d}r$$

More generally, expression (6) involves a special case of an integral which recurs in several sections of our work. It is :

$$R_{ns}^p = \int_0^\sigma \phi_n(r^p/\sigma^{p+1})\phi_s r^2 \mathrm{d}r + \int_0^\infty \phi_n(\sigma^p/r^{p+1})\phi_s\, r^2\, \mathrm{d}r = \sigma^{-1}(2\alpha\sigma/n)^{2n+1}\left\{1/(2n)\,!\right\}\times$$

$$\left[(2n+p)\,!\,/\left\{2\alpha\sigma/n)^{2n+p+1} - A_{2n+p}(2\alpha\sigma/n) + A_{2n-p-1}(2\alpha\sigma/n\right\}\right] . \quad (7)$$

Tables of the auxiliary functions σR_{ns}^p for selected values of p and n are given in an Appendix.

The total energy is the sum of the perturbation term (5) and the unperturbed energy given by (8) for hydrogen-like orbitals. The latter have radial factors identical with the Slater functions (4) for 1*s*, 2*p*, 3*d*, 4*f* . . . *i.e.*, when the azimuthal quantum number l has its maximum value of $(n - 1)$.

$$W_n = (\alpha/n^2)(\alpha/2 - Z_a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The procedure is to find the value of α for which the total energy given by (5) plus (8) is a minimum for selected value of the parameters σ, Z_a, and Z_s. The results are shown in Fig. 1. They allow a number of trends to be discerned. It has been noted that an orbital largely contained within the radius σ is little altered by the perturbing field, so that in the limits either of large σ or large Z_a we expect the effective charge increment $(\alpha - Z_a)$ to vanish. In harmony with this $(\alpha - Z_a)$ in Fig. 1 is less for $\sigma = 4$ than $\sigma = 3$ for given Z_a and Z_s values and it decreases in the order $Z_a = 0$, 1, and 2. The dependence upon the bond distance σ is sensitive in the model, and in real systems we expect that ligands joined by short bonds (*i.e.*, first-row elements) will cause larger perturbations than others. The values $\sigma = 3$ and 4 are roughly those for bonds between a first- and second-row element and two second-row elements respectively. Table 1 gives additional results illustrating the rapid decrease in $(\alpha - Z_a)$ with increasing Z_a : in general for $Z_a > 2n^2/\sigma$ contraction is negligible. The quantities P_a and P_α in Table 1 are the fractions of the electronic charge lying outside a sphere of radius $\sigma = 4$ in 3*d* orbitals of effective nuclear charges Z_a and α respectively. Contractions are large only when a significant amount of the unperturbed orbital lies outside the sphere.

TABLE 1. *Variation of the charge increment* $(\alpha - Z_a)$ *with* Z_a.

$\sigma = 4$, $Z_s = 0{\cdot}167$.

Z_a	P_a	α	P_α	$\alpha - Z_a$	Z_a	P_a	α	P_α	$\alpha - Z_a$
1	0·98	1·7	0·82	0·7	4	0·085	4·05	0·075	0·05
2	0·72	2·38	0·55	0·38	5	—	5·01	—	0·01
3	0·31	3·15	0·27	0·15	6	—	6·00	—	0

Small orbital contractions in our sense have long been known in simple systems for which detailed energy calculations have been made. For example, in H_2, Wang found that an effective nuclear charge of 1·166 units minimized the ground state energy in an

[5] Kotani, Amemiye, Ishiguro, and Kimura, "Tables of Molecular Integrals," Maruzen, Tokyo, 1955.

HLSP approximation. This result involves a consideration of all the energy terms and so depends strongly on the particular molecular state; for excited states of H_2 the effective nuclear charge may be less than unity. The relationship in detail between such changes in effective nuclear charge and those in our own work is thus slight.

The results in Fig. 1 show that the contraction of loosely bound orbitals may be large.

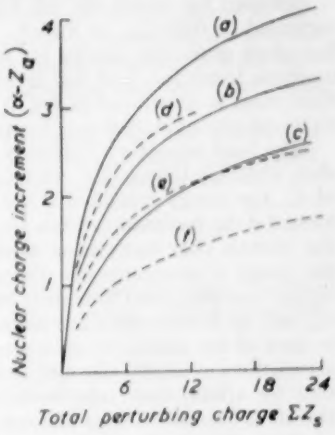


FIG. 1. *Values of the increment* $(\alpha - Z_a)$ *to the effective nuclear charge plotted as a function of the total perturbing charge* ΣZ_s. *The curves refer to different values of* Z_a, *the actual nuclear charge, and* σ, *the distance in a.u. of the perturbing charges from the nucleus.*

(*a*) $Z_a = 0$, $\sigma = 3$. (*b*) $Z_a = 1$, $\sigma = 3$.
(*c*) $Z_a = 2$, $\sigma = 3$. (*d*) $Z_a = 0$, $\sigma = 4$.
(*e*) $Z_a = 1$, $\sigma = 4$. (*f*) $Z_a = 2$, $\sigma = 4$.

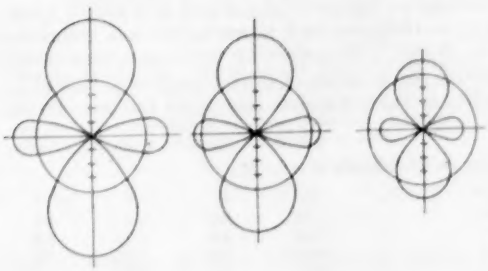


FIG. 2. *The contraction in an octahedral field of a* d_{z^2} *orbital of nuclear charge* $Z_a = 1{\cdot}5$. *The orbital is shown by the contour on which* $|\psi| = 0{\cdot}02$, *and the circle has a radius* $\sigma = 4$ *a.u., equal to the bond distance.*

Left-hand diagram: Field charges $Z_s = 0$.
Centre diagram: $Z_s = 0{\cdot}2$, $\alpha = 2$.
Right-hand diagram: $Z_s = 1{\cdot}5$, $\alpha = 3$.

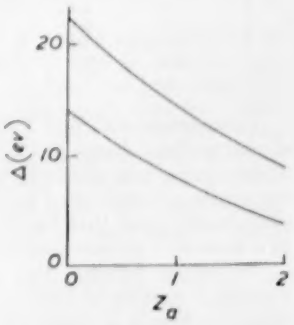


FIG. 3. *Increase in the energy of promotion from a non-projecting orbital to a 3d orbital of nuclear charge* Z_a *in the field of octahedral unit charges.*

Upper curve: *bond length* $\sigma = 3$ *a.u.*
Lower curve: $\sigma = 4$ *a.u.*

A 3*d* orbital with $Z_a = 1$ (as in the $3s3p^33d$ configuration of phosphorus) has its radial maximum at $r_m = 9$ a.u. In an octahedral field of unit charges at $\sigma = 3\ \alpha$ is 3·2 and the radial maximum is at 2·8 a.u., a value comparable with that of the orbitals of ligand atoms such as chlorine, and therefore compatible with covalent bonding. Typical magnitudes of orbitals before and after contraction are shown in Fig. 2.

An important point in a more general consideration of the bond possibilities is that the energy of promotion of the electron into the 3*d* orbital, if changed at all, is *increased* by the

perturbing field. The reason for this is that an inner, non-projecting, orbital is more stabilised than a projecting orbital, so that the excitation energy from one to the other is increased. The increase may be considerable. A 3*d* orbital of $Z_a = 1$ has a binding energy of 0·055 a.u. in the free atom and in the octahedral field of unit charges at $\sigma = 4$ it is 1·265 a.u., an increase of 1·21 a.u. A less projecting and more tightly bound 3*p* orbital is stabilised by almost the full $6Z_a/\sigma = 1{\cdot}5$ a.u., so that the excitation energy would be increased by 0·29 a.u., or 8·2 ev. This example is an extreme one, but it shows that the free-atom promotion energy to, say, P($3s3p^33d$) has little relevance to the conditions of molecule formation, and that an extra promotion energy of several volts may be required. This effect is illustrated in Fig. 3, which shows the incremental energy Δ for promotion to the 3*d* orbital plotted as a function of the nuclear charge Z_a.

The most important feature in Fig. 3 is the strong dependence of Δ on Z_a which shows that, although the overlap condition may be quite easy to fulfil over a considerable range of Z_a, the energy condition is not; and in particular we should not expect bonds to be formed if the free atom orbitals are very weakly bound indeed, *i.e.*, for $Z_a \simeq 0$, even though the orbitals after contraction would overlap sufficiently. It can safely be predicted that the energy of promotion into the valence state would require more energy than is supplied by the resulting bond formation under these conditions. Also crude methods of assessing Z_a, such as Slater's rules, are not good enough for accurate energy calculations of this kind in view of the sensitivity shown in Fig. 3, although they suffice for the rather insensitive calculations of orbital size and overlap. Moreover, we find that for energies, much more than for orbital sizes, later terms in the potential (3) are important. These remarks must therefore be read in their context as applying to the zero-th order approximation.

Contraction in Fourth Quantum Level Orbitals.—The radial maximum of a fourth quantum orbital of the Slater type occurs at $r_m = 16/Z_a$, or 16/9 times farther out than for a third quantum orbital of the same nuclear charge. We expect for this reason that orbital contraction will operate more strongly for the same values of the parameters σ, Z_s, and Z_a. This expectation is supported by the results in Table 2 which, except for the last column, are for $\sigma = 4$ a.u.

TABLE 2. *Contraction in 4f orbitals at* $\sigma = 4$.

Z_a	Z_s	α	$\alpha/4$	$\alpha^*/3$	Z_a	Z_s	α	$\alpha/4$	$\alpha^*/3$
0	0·25	1·5	0·4	0·5	1	1·0	3·9	1·0	1·1
0	0·5	2·5	0·6	0·7	1	2·0	4·6	1·15	1·3
0	1·0	3·5	0·9	0·9	2	0·25	3·0	0·75	0·9
0	2·0	4·35	1·1	1·2	2	0·5	3·6	0·9	1·0
0	4·0	5·1	1·3	1·4	2	1·0	4·2	1·05	1·2
1	0·25	2·4	0·6	0·7	2	2·0	5·0	1·25	1·4
1	0·5	3·1	0·8	0·9					

* For 3*d* orbitals at $\sigma = 3$.

Comparison with Fig. 1 shows, for example, that, for $\sigma = 4$ and $Z_s = 1$, a 3*d* orbital of unit nuclear charge has $\alpha = 2{\cdot}7$, compared with 3·9 for a 4*f* orbital. However a more useful comparison, shown in the last two columns of Table 2, is between the wave-function exponents α/n calculated at $\sigma = 4$ for the 4*f* orbital and at $\sigma = 3$ for the 3*d*. These are close, and suggest that for other principal quantum numbers n one might estimate values of α quite well by assuming the constancy of α/n evaluated for $\sigma = n$ a.u.

Secondary Effects.—Two equivalent electrons. In this and following sections we consider a number of factors which may be expected to modify the results obtained for a single electron in a spherically symmetrical field. It will be shown that within the range of values of the actual nuclear charge Z_a for which contraction is important, the modifying factors are relatively unimportant.

In phosphorus pentafluoride with the valence-state configuration $3s3p^33d$, and in the other cases of a single exterior electron, the model already discussed can be applied. In octahedral molecules of the sulphur hexafluoride type the central atom's valence state is $3s3p^33d^2$ with two equivalent and weakly bound *d* electrons and it is necessary to consider the influence of interelectronic repulsion. The analogous model is a helium-like two-electron system in the field of a bare nucleus surrounded octahedrally by positive charges.

Even in the $Z_s = 0$ limit we now have to consider both the actual nuclear charge Z_a and an effective nuclear charge which we shall call simply Z. In the one-electron case the two are the same. With two electrons Z becomes the effective charge required to minimize the total electronic energy, including interelectron repulsion. Z is less than Z_a on account of screening, as is well known in the treatment of the helium atom, and in the Slater theory of complex atoms. If we are to include electron repulsion explicitly in calculations of the properties of the two-electron system we must begin with the true nuclear charge Z_a and should find that, in the absence of a perturbing field, the energy is minimized by a value of α close to the Z given by Slater's rules. Interelectron repulsion alone causes a decrease in effective charge, *i.e.*, an orbital expansion, which will be opposed and finally overcome by the octahedral perturbation.

The energy of the two-electron valence-state may be found from the energies of stationary states of the same configuration. The energy of the appropriate valence state for two $3d_\gamma$ electrons is as follows, the d_ϵ orbitals being supposed inaccessible :

$$2I + F_0 - 6F_2 - 1{\cdot}5F_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in terms of the Slater parameters [6] F, and I, the single-electron binding energy. Evaluation of the F's leads to the expression $2I + 0{\cdot}0804\alpha$ for the total energy. Fig. 4 shows the terms I, $0{\cdot}0402\alpha$ and the perturbation energy separately plotted for the case $\sigma = 4$, $Z_a = 1{\cdot}5$, $Z_s = 1$.

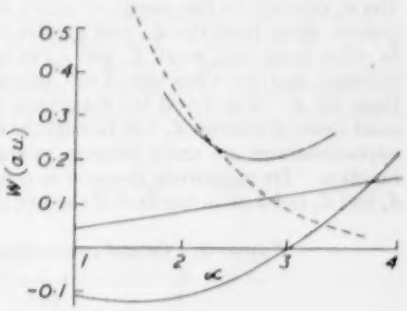


FIG. 4. *Energy terms for one of a pair of equivalent 3d electrons in the field of a nucleus of charge 1·5 surrounded by a regular octahedron of unit charges at a distance of 4 a.u. The lowest curve is the free-atom binding energy, the straight line is the interelectron repulsion term, 0·0402α, the broken curve is the zero-th order perturbation energy plus the constant 1·5 a.u., and the upper full line is the sum, showing a shallow minimum in the total energy at about α = 2·65.*

Without a perturbing field the energy is minimised by $\alpha = Z = 1{\cdot}14$, corresponding to a screening by one electron of the other equivalent to $1{\cdot}5 - 1{\cdot}14 = 0{\cdot}36$ electron, in close agreement with the Slater value of 0·35. The field being included, $\alpha = 2{\cdot}65$ compared with the value 2·85 for one electron, for which there is no repulsion term. One sees therefore that the screening correction for interelectron repulsion is reduced by the perturbing field. This is a general result which we shall use in the following way. Instead of using Z_a for the calculation we use the Slater value of effective nuclear charge; then α in the perturbing field is an underestimate of the formally correct value based on Z_a and explicit inclusion of interelectron repulsion. Since the under-estimation is small, usually much less than the upper limit 0·35, it is unimportant.

Higher approximations to the potential. Hitherto we have examined the effect on the the unperturbed atomic orbitals of the spherically symmetrical first term of the potential (3), which depends only upon the total charge $-6Z_s$ and its separation σ from the central nucleus. Second and later terms depend also upon the polar angles θ and φ. As is well known, an octahedral field does not remove the three-fold degeneracy of the p orbitals but splits the five d orbitals into a doublet (d_γ) and a triplet (d_ϵ) of which the doublet is lower under our conditions of positive field sources. The second term of (3) causes the major part of this splitting. The energies of the split components may differ considerably and

[6] Condon and Shortley, "The Theory of Atomic Spectra," Cambridge Univ. Press, 1953, p. 202.

orbital contractions must be calculated separately for them. In terms of the integrals (7) we have for the perturbation energies :

$$d_\epsilon : -(Z_s/\sigma)\left\{6\sigma R^0_{33} - (2/3)\,\sigma R^4_{33}\right\}$$
$$d_\gamma : -(Z_s/\sigma)\left\{6\sigma R^0_{33} + \sigma R^4_{33}\right\} \qquad \ldots\ldots\ldots \quad (10)$$

The first term, common to both expressions, has already been discussed at length. The second term is now added and the total energy minimized, giving values of α for d_ϵ and d_γ. Typical results for $Z_a = 1{\cdot}5$, $\sigma = 4$ a.u., are shown in Table 3. The zero-th order term σR^0_{nn}, increases monotonically with $\alpha\sigma$, and it must increase the effective charge. The term σR^4_{33}, tabulated in an Appendix, approaches zero both at small and at very large values of $\alpha\sigma$, passing through a maximum at $\alpha\sigma = 10{\cdot}5$. Near this maximum it varies slowly, and its influence on the rate of change of the total energy is correspondingly small. This is the reason why Table 3 shows no change in α from the inclusion of the second term in the potential in the first example. For $\sigma = 4$ the maximum in σR^4_{33} occurs at $\alpha = 2{\cdot}625$, so that if the zero-th order term gives $\alpha > 2{\cdot}625$ the second term of the potential will decrease α. This is too small an effect to be apparent in the first case in Table 3, but appears in the second, where the larger charges $Z_s = 4$ cause larger magnitudes throughout. This accounts for the fact that the d_γ orbitals, which are the more stable, have a lower α value. The d_ϵ orbitals, in the energy of which the σR^4_{33} term appears with negative sign, have a greater value than the d_γ, and greater than the zero-th order value in the last column. In other cases (*viz.*, small Z_a and Z_s) in which the energy corrections are less, this trend is reversed, and, for α less than 2·625, the second term increases α values for d_ϵ and decreases them for d_γ. For $\sigma = 3$ the maximum in σR^4_{33} is at the larger value $\alpha = 3{\cdot}5$, so that in most cases of interest d_γ will be slightly more contracted than d_ϵ. These effects of higher approximations are small because, in the interesting range of α, σR^4_{33} is a slowly varying function. Its magnitude however is considerable, and the splitting caused by it between d_ϵ and d_γ is 4·3 ev in the first of the two examples quoted in Table 3.

TABLE 3. *Orbital contraction in an octahedral field* $Z_a = 1{\cdot}5$, $\sigma = 4$ *a.u.*

Z_s	α (d_γ)	α (d_ϵ)	α (zero-th order)
1	2·75	2·75	2·75
4	3·5	3·75	3·6

The relative insignificance of the second term in the potential applies only to small values of Z_a. Large values of Z_a bring in large values of $\alpha\sigma$, and it becomes important that σR^4_{33} falls off more slowly at large $\alpha\sigma$ than does σR^0_{33} so that the former becomes predominant. For $Z_a = 6$, $\sigma = 4$, and field charges $Z_s = 4$ the values of α are $\alpha(d_\gamma) = 5{\cdot}6$ and $\alpha(d_\epsilon) = 6{\cdot}3$, both being determined by the second term in the potential. The interest in such extreme cases is only formal because at $Z_a = 6$ the orbital is already suitable for covalent-bond formation, and the change in size caused by the perturbation has a negligible effect on its overlapping power.

Values of the quantity σR^4_{44}, tabulated in an Appendix, allow the analogous calculations to be performed on orbitals of principal quantum number 4; we shall not discuss these in detail. The maximum value of σR^4_{44} is at $\alpha = 4{\cdot}5$ for $\sigma = 4$, allowing the general conclusion that over most of the important range the second term in the potential will increase α for d_γ orbitals. Also because the variation is slow, the effect of this term is small as in the 3*d* calculation.

The reasons for the particular types of variation in α which higher terms induce are inherent in the problem. The point charges which surround the central atom attract the electron in the central atom's orbital. If this orbital is small compared with the radius of the charges it will tend to be expanded; if it is large it will be contracted; and the transition between these forms of behaviour will occur at a value of α for which the radial maximum of the orbital occurs at, or near, the charge radius σ. Now the radial maximum is at $r_m = n^2/\alpha$, where n is the principal quantum number of the orbital; equating r_m with σ

we find that the transition between orbital expansion and contraction is at $\alpha\sigma = n^2$, or at 9 a.u. for a 3 quantum orbital and 16 a.u. for a 4-quantum orbital. These values are not exact because the radial maximum is not exactly the measure of the quantity associated with the orbitals which determines whether they are drawn outward or inward by the field, but it is fairly close. A more precise measure is the value $\alpha\sigma$ at which the integrals of the later terms in the expansion have their maxima, *viz.*, $\alpha\sigma = 10{\cdot}5$ and 18 for third- and fourth-quantum orbitals respectively. Under the conditions of our problem the orbitals always require contraction to minimize their energy, and the zero-th term in the expansion of the potential overwhelms all others; this shows no maximum, and consequently the presence of the maximum only shows itself through the minor modifying effects which later terms in the potential exert.

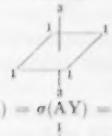
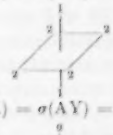
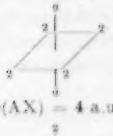
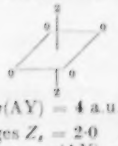
Fields of lower symmetry. These may be produced by variations either in the charges Z_a or in the distances between the central atom and the ligands or in both. To simulate conditions in, for example, AX_4Y_2 molecules such as SF_4Cl_2 presumably both are required, but the effects of the variations are best examined separately. The first example is a *trans*-octahedral array consisting of two charges Z_{ax} and four Z_{rad}, all at the same distance σ.

The potential is :

$$V_{r<\sigma} = -(2Z_{ax} + 4Z_{rad})/\sigma - \sqrt{(2/5)}\,\Theta_2^0(2Z_{ax} - 2Z_{rad})(r^2/\sigma^3) - \sqrt{(2/9)}\,\Theta_4^0(2Z_{ax} + 1{\cdot}5Z_{rad})(r^4/\sigma^5) - (35/16)\sin^4\theta\cos 4\varphi\, Z_{rad}(r^4/\sigma^5) - \quad . \quad . \quad (11)$$

together with analogous expression for $V_{r>\sigma}$. The perturbation energy corresponding to the potential (11) can be found by using tables in the Appendix. One finds that in the important range of Z_a the major contribution to the energy is from the spherically symmetrical term which represents the potential of a charge $2Z_{ax} + 4Z_{rad}$ uniformly spread over a spherical surface of radius σ. The later terms in the potential (11) remove

TABLE 4. *Effective nuclear charge in* trans-AX_4Y_2 *fields.*

Field	Z_a	$\alpha(d_{z^2})$	$\alpha(d_{xz}, d_{yz})$	$\alpha(d_{x^2-y^2})$	$\alpha\ (d_{xy})$
	1·5	3·0	3·2	3·05	3·25
	2·0	3·1	3·35	3·15	3·5
$\sigma(AX) = \sigma(AY) = 4$ a.u.					
	1·5	2·95	3·25	3·0	3·1
	2·0	3·08	3·48	3·10	3·33
$\sigma(AX) = \sigma(AY) = 4$ a.u.					
	1·5	3·0	3·0	2·95	3·0
	2·0	3·15	3·15	3·05	3·15
$\sigma(AX) = 4$ a.u.					
	1·5	2·65	2·65	2·65	2·65
	2·0	2·85	2·9	2·9	2·9
$\sigma(AY) = 4$ a.u.					
Equal charges $Z_a = 2{\cdot}0$	1·5	3·6	3·55	3·3	3·55
$\sigma(AX) = 4$ a.u. $\sigma(AY) = 3$ a.u. ...	2·0	3·7	3·65	3·4	3·75
Equal charges $Z_a = 2{\cdot}0$	1·5	3·65	3·8	3·75	3·85
$\sigma(AX) = 3$ a.u. $\sigma(AY) = 4$ a.u. ...	2·0	3·8	4·1	3·9	4·1

most of the degeneracy of the orbitals, giving four components, namely d_{z^2}, d_{xy}, $d_{x^2-y^2}$, and d_{xz}, d_{yz}, the last two remaining degenerate. For each component the energy must be minimized with respect to the exponent α, for given values of the parameters Z_a, Z_x, and σ. Some values are given in Table 4. In connexion with binding in molecules,

d_{z^2} and $d_{z^2-y^2}$ are of special interest, the former being concerned mainly in the axial bond orbitals and the latter with p_x, p_y, and s in the radial orbitals.

The second extreme representation of asymmetrical molecules is in terms of variable bond lengths σ, with the same Z_s for all ligand groups. The important comparison is now between different molecules such as AX_4Y_2, AX_2Y_4, and the trend is illustrated by reference to ligands X and Y having the same charge Z_s but separated from the central atom by 3 and 4 atomic units respectively. Results are shown in the last two sets of Table 4. One sees that the effect of 2 or 4 of the more closely held ligand X on the exponent α is not too different from a linear interpolation between the extremes AX_6 and AY_6. The effect is dominantly isotropic with only minor variations between different orbitals. Thus contraction is greater in all directions for the presence of some groups held by short bonds. This might be important in molecules in which, by analogy with the properties of the model, one would expect that one or more groups held by short bonds (*e.g.*, first-row elements) would extend their influence to all the groups present and so to strengthen all the bonds.

To complete this consideration of the less symmetrical fields we should consider asymmetry developed by differences of charge and distance together. However this hardly seems necessary. The effect of charge asymmetry is small compared with the effect of the same total charge uniformly distributed, and smaller than the effect of changes in bond length. One finds that changing σ from 4 to 3 causes the same change in α as doubling the charges Z_s at a constant $\sigma = 4$. Thus where both charges and distances alter, the former may in general be neglected; and if only the charges vary it is clear that the consequent variations in α from orbital to orbital are small.

Interaction of the 3d with Other Atomic Wave Functions.—A full solution of the perturbation problem calls for an expansion in a complete set of functions, such as the hydrogen-like atomic functions of nuclear charge $Z_a + \delta$ referred to earlier. The effect of this is to allow flexibility in the form of the radial wave function and so to distribute the electronic charge between the central nucleus and the perturbing nuclei in the manner required to minimise the energy. Such an expansion is not of course unique: variation in the radial function provides for a charge drift which could be approximated in other ways, such as by using a wave function initially which allowed some migration of the electron into orbitals at the perturbing centres.

In the regular octahedral field, the number of different atomic wave functions able to participate in the expansion is reduced by symmetry. In this field a d atomic wave function has components which transform as do the E and T_1 representations of the octahedral group. The same representations occur in wave functions of azimuthal quantum number 4, 6, 8 . . . so that the lowest wave function of other than d symmetry appearing in the expansion is the $5g$. The separation between orbitals $n = 3$ and $n = 5$ in the perturbing fields is several electron-volts and the influence of this orbital is negligible under this and the other conditions of the problem. The only important interconfigurational mixing is with other orbitals of d symmetry, and of these the $4d$ is most prominent, on account of its being closest in energy to the $3d$.

We consider the wave function (12) in terms of which the importance of $3d$ and $4d$ mixing may be studied :

$$\Psi(\alpha, \chi) = \phi_3 \cos\chi + \phi_4 \sin\chi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

The $3d$ and $4d$ wave functions are given the same effective charge α. The energy may be expressed as follows, the new integrals $\mathfrak{A}$ and $\mathfrak{B}$ being tabulated in an Appendix.

$$W(\chi, \alpha\sigma) = \cos^2\chi\left\{W_{3d}(\alpha\sigma) - (6z_s/\sigma)\, R^0_{23}(\alpha\sigma)\right\} + \sin^2\chi\left\{W_{4d}(\alpha\sigma) - (6Z_s/\sigma)\mathfrak{A}(\alpha\sigma)\right\} - \sin 2\chi(6Z_s/\sigma)\mathfrak{B}(\alpha\sigma) \quad . \quad (13)$$

The values of $\cos^2\chi$ and α which make the energy a minimum under the conditions $Z_a = 1$ and $\sigma = 4$ are given in Table 5. The examples, which are representative, show a marked energy depression by configuration mixing (1·8, 2·6, and 2·9 ev respectively) but only a

small change in α. Moreover the weight of the 3*d* function, given by $\cos^2\chi$, remains high, showing that the properties of the mixed wave function will be dominated by the 3*d* component. Thus we may expect that, for example, values of the overlap integral derived from a single contracted orbital will be close to values from the more complicated forms. In a field of lower symmetry, mixing will doubtless play a somewhat larger part.

TABLE 5. *The effect of* 3*d and* 4*d mixing for* $Z_a = 1$, $\sigma = 4$.

Z_s	α	$W_{min} + 6Z_s/\sigma$	$\cos^2\chi$	α ($\chi = 0$)	$W + 6Z_s/\sigma$ ($\chi = 0$)
1	2·65	0·17 *a.u.*	0·9	2·75	0·235 *a.u.*
2	2·85	0·245	0·9	3·05	0·34
4	3·15	0·345	0·9	3·45	0·45

Summary of Conclusions based on the Model.—(i) Slater orbitals of principal quantum numbers 3 and 4 with free-atom effective nuclear charges in the range 0—3 are strongly contracted by point charges at a distance σ equal to an average bond length. After contraction the effective nuclear charges α are usually in the range 1·5—5. Orbitals of principal quantum number $n = 4$ are more affected than $n = 3$.

(ii) It may be inferred that similar but diminishing effects will occur for orbitals of $n = 2$ and $n = 1$, and increasing effects for $n = 5$ and 6.

(iii) For low values of free-atom effective nuclear charge the predominant effect is isotropic, affecting all orbitals with the same radial dependence whatever their angular properties. Secondary directional effects are small, even in fields such as the axial field of two point charges. In the secondary effect orbitals directed towards the field charges are more contracted than others if very loosely bound, and less contracted otherwise; the transition occurs for $n = 3$ orbitals at $\alpha\sigma = 10{\cdot}5$ and for those of $n = 4$ at $\alpha\sigma = 18$.

(iv) Because the contraction is mainly isotropic orbitals capable of π-bonding are contracted nearly to the same degree as σ-bonding orbitals.

(v) The energy of electron promotion in the presence of the field is greater than the free-atom promotion energy by an increment Δ depending on the distance σ, the charges Z_s of the field sources and the free-atom effective charge Z_a. The increment for $Z_a \simeq 0$ is probably greater than the free-atom promotion energy. For values of Z_a appropriate to the 3*d* orbitals of S and P the increment may be about 5 ev in the zero-th order approximation, but less when terms of higher order are included.

Application to Molecules.—The properties of the model systems may be calculated precisely or, if approximations are made, their effect can be foreseen. However, use of results for the model to interpret molecular properties requires assumptions of a far-reaching kind. Some of them inherent in the overlap approximation have been discussed.[1] Others concern mainly the use of Slater orbitals for the central atom and simulation of the atomic fields of the ligand atoms by the coulomb field of a point charge. Our discussion is confined to the particular question of the feasibility of covalent bonding after allowance for increase in overlap of the contracted orbital of a central atom with the orbitals of the ligand atoms. We shall not attempt to deal with the final determining factor in bonding, namely, the energy, since the relation between overlap and bond energy is not well established.

Slater functions are not very close approximations to self-consistent-field *d* orbitals, but this is not serious in calculations of overlap integrals which, at best, can serve only as a rough guide to the bonds likely to be formed. As applied to our present calculations the position is no worse; indeed it is likely to be somewhat better since we are concerned to establish a specific effect upon highly projecting orbitals and only the finer quantitative aspects of this depend upon the form of the orbital. Equally, it is of secondary importance for overlap calculations whether, the form of the orbitals being accepted, the exponents given by Slater's rules for free atoms have a precise quantitative significance. It will be seen in the work described in earlier sections that the value of α in the contracted orbital varies more slowly than the Z_a of the free-atom orbital, so that an error in the latter is cushioned. Finally, it has to be ensured that the Slater exponent can be identified with Z_a/n, where n is the principal quantum number, in the model. Treating this point

first, we note that the Slater exponents are in principle derived by minimizing the total energy of an atom. This includes exchange as well as coulomb-type terms. If, as for example in the $3s3p^33d$ configuration of P, we have a single electron exterior to all the rest the exchange interactions of this electron are very small, and the effect of all the other electrons on it differs little from the effect of the same total electronic charge amalgamated with the nucleus. In this case we are quite justified in identifying the Slater effective charge with the actual charge Z_s on the nucleus in the model. If there are two equivalent projecting electrons as in $3s3p^33d^2$ the Slater value of the effective charge may be identified with Z_s only when allowance is made for the mutual repulsion between the two electrons, as described earlier, and when exchange integrals of the other electrons with the outer pair may be ignored. The case would be quite different for an inner electron; there the potential field is not even roughly that of point charge but has substantial non-central coulomb and exchange contributions strongly configuration-dependent, and the behaviour of the electron could not be represented at all well in a one-electron model with the same nuclear charge. It turns out that only in the circumstances of a highly screened and loosely bound exterior electron can our model be applied; and fortunately this is the case of interest.

*The Field of Ligand Atoms.**—To apply the model to molecules also makes it necessary to represent the field of a ligand atom by that of a point charge. The approximation made in doing this can be brought out by considering a case intermediate in complexity between the model and real systems. This is a central hydrogen-like atom with, as usual, a loosely bound electron surrounded, not by point charges, but by other hydrogen-like atoms, introducing the possibility of bonding between the electron of the central atom and those of the surrounding atoms. The potential of the ligands now consists of the attraction of their nuclei minus the coulomb repulsions of the ligand's electrons plus exchange terms. Evidently the dependence on distance of this composite potential will not follow the r^{-1} law at all closely, and the parameter Z_s used in the model as the perturbing charge of the ligand can be no more than the parameter of a coulomb field which is equivalent in some sense to the true atomic field. The same holds in complex atoms. It is clear that at any point in the field of an atom there is a value of Z_s which will give the value of the potential at that point provided only that the field is spherically symmetrical, and another which will give the field strength, but the values of each vary with r. Values of these quantities are given in calculations of the self-consistent fields of atoms and may be used in a useful comparison of the halogen atoms F, Cl and Br. For this purpose Table 6 compares values of Z_p, the potential-determined nuclear charge, and Z_f, the field-determined nuclear charge for the halogens each at its single-bond covalent radius.

TABLE 6. *S.C.F. Effective charges of the halogens at the covalent radius.*

	Covalent radius (a.u.)	Z_p	Z_f	Ref.
F	1·21	0·7	2·6	8
Cl	1·87	0·8	3·1	9
Br	2·16	0·7	3·1	10

Differences between the halogen atoms should not be expressed primarily as differences in the charge parameter Z_s since at the respective covalent radii the charges are nearly the same and show no clear trend. We shall therefore assign to the halogens the same value Z_s, and treat this as a parameter, taking values in the range 0·25—4·0, which includes the likely values both of Z_p and Z_f in Table 6. The differences in behaviour between the halogens emerge as the result of different separations from the central atom and not of different perturbing charges. The contraction is quite sensitive to changes in the distance

* Clearly the effect of ligand atoms is related to their electronegativity; but electronegativities cannot be used directly, since separate values are required for effective charge and bond length. These two are amalgamated in the concept of electronegativity.[7]

[7] Pritchard and Skinner, *Chem. Rev.*, 1955, **55**, 745.
[8] Brown, *Phys. Rev.*, 1933, **44**, 214.
[9] Hartree, Kronig, and Paterson, *Physica*, 1933, **1**, 895.
[10] Arnot and McLaughlan, *Proc. Roy. Soc.*, 1934, *A*, **146**, 662.

parameter σ, as has already been pointed out, and, since the bond-length differences are considerable, the contractions vary substantially from F to Cl, and from Cl to Br. We should expect different Z_s values for elements in different Periodic Groups, but variations in bond lengths should still play the more important part. It must be emphasized that this discussion of actual values for Z_s is tentative. The fact that the ligand fields are not truly coulombic makes the choice of the "equivalent" coulomb parameter rather uncertain.

The domain of application of the model is, broadly, to those molecules for which covalent binding requires participation by loosely held *d* orbitals. The simplest are those with 3*d* orbitals, for example, the halides of second-row elements and certain complex ions such as AlF_6^{3-}; and with 4*d* orbitals there are analogous halides and ions and as well the large and important class of transition-metal complexes with incomplete 3*d* shells. In some of these, both 3*d* and 4*d* electrons may be concerned: the 3*d* by their electrostatic stabilization in the crystalline field, and the 4*d* in covalent binding. On account of their additional complexity we postpone dealing with these molecules and confine attention to the simple examples for which, moreover, overlap integrals are available.

In a following section we apply our work to two specific cases, namely, the halides of sulphur and phosphorus. The application of the model to these molecules has the following features: (i) for the central atom we use the effective nuclear charge calculated from Slater's rules as the actual nuclear charge of a hydrogen-like orbital, treating inner electrons as fused into the nucleus. This applies to a single exterior *d* electron as in $P(3s3p^33d)$; with two equivalent electrons, as in $S(3s3p^33d^2)$, interelectronic effects are allowed for either by using the Slater effective charge for the configuration $3s3p^33d$ and including interelectron repulsion explicitly or, a little less precisely, by using the Slater exponent straightforwardly for the two-electron case and allowing the repulsion to be taken up in the extra screening correction. (ii) For the ligand atoms we retain the fiction of a coulomb field but compute for a wide range of the coulomb parameter Z_s. The same charge parameter is used for all halogens, differences being allowed to appear through the variations in internuclear spacings σ.

Application to molecules PX_5 *and* SX_6. The bond lengths in phosphorus pentafluoride and pentachloride are approximately 2·9 and 4·0 a.u. Ignoring small effects such as higher order terms in the potential, we work out the contractions as already discussed, for a range of charge parameters Z_s and equating σ to the bond length. The calculations are summarized in Table 7, in which $\alpha/3$ is the exponent of the contracted 3*d* orbital. Since our results depend only on the total charge $\sum Z_s$, the octahedral field results for $Z_s = 0{\cdot}25$ apply directly to the trigonal bipyramid for $Z_s = 0{\cdot}30$ and the same bond lengths.

TABLE 7. *Contractions and* p_s–d_s *overlaps in* PF_5 *and* PCl_5.

	PF_5			PCl_5		
Z_s	σ	$\alpha/3$	S	σ	$\alpha/3$	S
0	—	0·33	0	—	0·33	0
0·3	3	0·7	0	4	0·6	0
0·6	3	0·9	−0·01	4	0·8	0·1
1·2	3	1·1	0·05	4	0·9	0·17
2·4	3	1·3	0·12	4	1·0	0·2
4·8	3	1·5	0·17	4	1·1	0·22

In Table 7 the P–F bond length is taken as 3·0 a.u. to use values already tabulated. The overlaps are $2p_s$–$3d_s$ for PF_5 and $3p_s$–$3d_s$ for PCl_5; the latter has been tabulated [1] and the former is given in an Appendix. For all Z_s the phosphorus orbital is more contracted in the pentafluoride than in the pentachloride, and the overlap associated with the contracted orbitals is comparable in the two examples although distinctly greater in the second. Small differences in overlaps may or may not be significant for bond strengths; the more important points are, first, that contraction is bigger for the fluoride than for the chloride for the same effective charges Z_s, and, secondly, that the *d* overlap becomes comparable with the *s*–*p* and *p*–*p* overlaps for Z_s values within the physically reasonable range. For example in the pentachloride the P(*s*)–Cl(*p*) overlap is 0·24 and the P(*p*)–Cl(*p*)

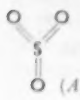
overlap is 0·28, both little greater than the *p*–*d* values given at the end of Table 7. The sp^3d covalent bond model in phosphorus pentachloride becomes tenable therefore once the contraction has been allowed for; and similar arguments apply to the pentafluoride.

In the hexahalides of sulphur we take $\sigma = 3$ a.u. for the fluoride and $\sigma = 4$ for the hypothetical chloride. The overlaps are found by interpolation in the tabulated values (Table 8). As before, the *d* overlap becomes considerable when the contraction is taken into account; it is comparable to the overlap of *s* and *p* orbits of S.

Table 8.

	SF_6			SCl_6		
Z_s	σ	$\alpha/3$	S	σ	$\alpha/3$	S
0	—	0·55	0	—	0·55	0
0·25	3	0·9	0·0	4	0·7	0
0·5	3	1·0	0·05	4	0·8	0·14
1·0	3	1·1	0·07	4	1·0	0·15
2·0	3	1·3	0·12	4	1·1	0·18
4·0	3	1·5	0·17	4	1·2	0·20

π-Bonding. Even in unsymmetrical fields all the *d* orbitals are contracted to about the same extent. For example in the "square" field of 4 equal charges $Z_s = 2$, one finds $\alpha(d_{z^2}) = 3{\cdot}15$, $\alpha(d_{x^2-y^2}) = 3{\cdot}05$, $\alpha(d_{xz},d_{yz}) = 3{\cdot}15$. The last orbitals are used for π bonding in a square molecule, and the near equality of effective charge with the σ-bond orbital shows that an environment which prepares diffuse *d* orbitals for participation in σ-bond formation will allow π-bonding also if other conditions are met, such as availability of orbitals on the ligand atom. An example in which such π-bonding is important is sulphur trioxide, although here it is not necessary to invoke *d* participation in the σ-framework. If the sulphur valence state is taken as $3s3p^43d$ or $3s^23p^33d$ three σ-bonds hold the trigonal shape, and one π-bond can be formed by using one of $3d_{xz}$ and $3d_{yz}$ or $3p_z$, the π-bond being shared between three sites. Alternatively if two electrons are to be promoted into the configuration $3s3p^33d^2$, three sp^2 bonds are supplemented by three pd^2 π-bonds. Both possibilities have of course been long recognized; but we can now support them by the consideration that the *d* orbitals concerned are capable of substantial overlaps with the $2p\pi$ orbitals of oxygen. With a value of $Z_s = 1{\cdot}0$ chosen to use available results, we find $\alpha(d_{xz}) = 2{\cdot}8$. The $3d_\pi$–$2p_\pi$ overlap integral for the S–O bond is **0·26**, a value which would be increased in a *p*–*d* hybrid. One sees therefore that the overlap requirements implicit in the suggestion of double bonding are amply met. The gain from the second electron promotion amounts to two extra π-bonds, and a strengthening even of the first, so that one might expect the sp^3d^2 valence state to be attained in this molecule, as in the structure (*A*).



(*A*)

We thank Dr. I. G. Ross for his helpful comments on the manuscript.

Appendix I. *Auxiliary functions defined in equation* (7).

$\alpha\sigma$	σR^0_{22}	σR^1_{23}	σR^0_{23}	σR^2_{33}	σR^1_{33}	σR^0_{24}	σR^2_{44}	σR^4_{44}	$\mathfrak{A}$ *	$\mathfrak{B}$ †
2·5	0·4133	0·1976	0·1088	0·0679	0·0470	0·3563	0·3123	0·0453	0·0110	0·3048	0·1125
3·0	0·4915	0·2723	0·1692	0·1158	0·0854	0·4261	0·3742	0·0766	0·0259	0·3571	0·1291
3·5	0·5656	0·3497	0·2368	0·1727	0·1333	0·4941	0·4357	0·1169	0·0479	0·4071	0·1411
4·0	0·6341	0·4249	0·3061	0·2334	0·1861	0·5593	0·4958	0·1655	0·0787	0·4514	0·1477
4·5	0·6961	0·4939	0·3714	0·2922	0·2385	0·6208	0·5541	0·2203	0·1175	0·4928	0·1486
5·0	0·7511	0·5538	0·4286	0·3447	0·2859	0·6778	0·6098	0·2785	0·1616	0·5317	0·1447
6·0	0·8394	0·6408	0·5098	0·4189	0·3531	0·7757	0·7107	0·3930	0·2559	0·6074	0·1257
7·0	0·9011	0·6838	0·5433	0·4467	0·3771	0·8510	0·7948	0·4879	0·3381	0·6831	0·0989
8·0	0·9416	0·6912	0·5373	0·4354	0·3639	0·9052	0·8604	0·5503	0·3917	0·7554	0·0719
9·0	0·9667	0·6743	0·5053	0·3988	0·3271	0·9419	0·9087	0·5776	0·4115	0·8211	0·0490
10·0	0·9817	0·6434	0·4598	0·3501	0·2795	0·9657	0·9424	0·5749	0·4014	0·8746	0·0316
12·0	0·9949	0·5676	0·3616	0·2511	0·1863	0·9890	0·9792	0·5126	0·3278	0·9470	0·0116
15·0	0·9994	0·4647	0·2455	0·1444	0·0929	0·9984	0·9963	0·3807	0·1958	0·9882	0·0020
20·0	1·0000	0·3500	0·1399	0·0629	0·0314	0·9999	0·9999	0·2243	0·0729	1·0000	0·0002

* $\mathfrak{A} = 4{\cdot}5\sigma R^0_{22} - 10{\cdot}5\sigma R^0_{34} + 7\sigma R^0_{44}$. † $\mathfrak{B} = 1{\cdot}974(\sigma R^0_{22} - \sigma R^0_{34})$.

APPENDIX 2. *Overlap integrals:* $S(2p_z\text{–}3d_z)$.

p/t *	−0·5	−0·4	−0·3	−0·2	−0·1	0·0
2	−0·1688	−0·2411	−0·3106	−0·3698	−0·4124	−0·4338
3	−0·1042	−0·1349	−0·1610	−0·1831	−0·2021	−0·2183
4	−0·0216	0·0078	0·0105	0·0268	0·0346	0·0299
5	0·0382	0·0770	0·1182	0·1539	0·1770	0·1826
6	0·0675	0·1113	0·1548	0·1917	0·2175	0·2286
7	0·0740	0·1111	0·1454	0·1739	0·1949	0·2069
8	0·0675	0·0938	0·1163	0·1343	0·1484	0·1586
9	0·0558	0·0719	0·0842	0·0936	0·1017	0·1093
10	0·0433	0·0517	0·0570	0·0607	0·0646	0·0697

p/t *	0·1	0·2	0·3	0·4	0·5
2	−0·4313	−0·4040	−0·3540	−0·2859	−0·2076
3	−0·2303	−0·2352	−0·2289	−0·2077	−0·1705
4	0·0118	−0·0169	−0·0495	−0·0770	−0·0900
5	0·1684	0·1354	0·0882	0·0357	−0·0103
6	0·2226	0·1985	0·1573	0·1038	0·0473
7	0·2083	0·1968	0·1707	0·1300	0·0792
8	0·1642	0·1630	0·1519	0·1277	0·0903
9	0·1162	0·1210	0·1205	0·1106	0·0878
10	0·0761	0·0832	0·0886	0·0884	0·0777

* Notation as in ref. 1.

DEPARTMENT OF PHYSICAL CHEMISTRY,
THE UNIVERSITY OF SYDNEY.
DEPARTMENT OF CHEMISTRY,
THE N.S.W. UNIVERSITY OF TECHNOLOGY.

[*Received, September 20th*, 1956]

---

956. *Hydroaromatic Steroid Hormones. Part V.* Some* D-*Homo*-18 : 19-*bisnorsteroids.*

By A. J. BIRCH and HERCHEL SMITH.

Syntheses of (±)-D-homo-18 : 19-bisnortestosterone † (II; R = H) and (±)-D-homo-18 : 19-bisnorandrostane-3 : 17-dione † (I; R = H) from 1 : 2 : 7 : 8-tetrahydro-3 : 10-dimethoxychrysene [1] are described.

IN Part I [2] the reasons were given for believing that steroids lacking one or both of the 18- and 19-methyl groups should be biologically active, provided the stereochemistry is correct. This belief has been strengthened by demonstration of the androgenic activity of 19-nortestosterone,[2,3] which was the first active androgen made by total synthesis, and later of other hormone analogues [4,5] all made by essentially the same process involving the reduction of an aromatic ring by means of metal–ammonia–alcohol reagents.[6] Recent work on the biosynthesis of steroids [7] shows that the angular methyl groups are essentially relics of the isoprene units in precursors, providing further grounds for believing that such groups may not be necessary or even desirable for biological activity. Several 19-norsteroid hormones are in fact more biologically active than are the steroids themselves.[4,5]

Alteration of the skeleton may result not only in alteration of the intensity of biological activity but in alteration in ratios of activities when a hormone possesses more than one type of activity. Male hormones in particular have an anabolic activity which is of great therapeutic interest and would in an ideal anabolic agent be divorced from the typical

* Part IV, Birch and Harrisson, *Austral. J. Chem.*, 1955, **8**, 519.

† These compounds are given steroid numbering to facilitate comparison with this series; various intermediates are numbered systematically as chrysene derivatives.

[1] Collins and Smith, *J.*, 1956, 4308.
[2] Birch, *J.*, 1950, 367.
[3] Birch, *Ann. Reports*, 1950, **47**, 210.
[4] Miramontes, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 4440.
[5] Sandoral, Miramontes, Rosenkranz, Djerassi, and Sondheimer, *ibid.*, p. 4117; 1955, **77**, 148.
[6] Birch, *J.*, 1944, 430, and later papers; Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5355.
[7] *E.g.*, Clayton and Bloch, *J. Biol. Chem.*, 1956, **218**, 305, 309.

androgenic activity. That such a separation of activities is possible can already clearly be seen in the norsteroid series. 19-Nortestosterone has an anabolic : androgenic ratio of about 2·5, compared with testosterone; and the D-homo-19-nortestosterone reported in Part IV * has a ratio of about 6. Recently [8] it has been reported that for 17-ethyl-19-nortestosterone the ratio is 16. We now report further work aimed at examining the effect on biological activity of omitting the 18-methyl group, with retention of the natural steroid stereochemistry.

There seems reason to believe that *cyclo*pentenophenanthrene derivatives would be active in absence of the 18-methyl group, provided the C–D ring junction is *trans*.[2] In view of the difficulty of synthesising such compounds we have initially been concerned with D-homo-18-norsteroids with a readily attainable C–D-*trans* junction. Since this suggestion regarding activity was originally made,[2] some confirmation has been obtained by W. S. Johnson and his collaborators who showed that (±)-D-homo-18-norandrostane-3 : 17-dione [9] (I; R = Me) is as active androgenically as (±)-androstane-3 : 17-dione itself. However, it later appeared that D-homo-18-nortestosterone [10] (II; R = Me) is inactive although the acetate and propionate possess one-tenth of the androgenic activity of the corresponding testosterone derivatives. Our own initial attempts [11] in this field were unsuccessful owing to failure to prepare appropriately substituted chrysene derivatives, but a mixture of steroisomers of what is probably an 11-hydroxy-D-homotestosterone (III) was shown to possess weak androgenic activity.[12]

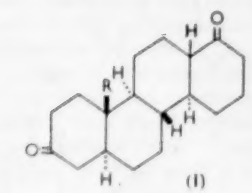
After the start of our work on the synthesis of the ketone (II; R = H), Johnson, Dehn, and Chinn [13] reported its synthesis by a rather difficult route and stated that it was inactive as an androgen. It appeared to us desirable, however, to examine its biological activity further and to develop methods which could be adapted to the preparation of related compounds carrying the side-chains characteristic of other hormones. In view of the great structural specificity already demonstrated for androgenic activity there is clearly still some possibility that activity will be found in analogues of other hormones. Also, since the diketone (I; R = Me) is androgenic whilst the keto-alcohol (II; R = Me) is not, we have prepared the analogue (I; R = H) for comparison with the compound (II; R = H).

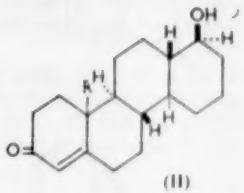
The ready synthesis of the desired starting material, 1 : 2 : 7 : 8-tetrahydro-3 : 10-dimethoxychrysene (IV) is described elsewhere.[1] * Reduction of this compound with sodium and boiling butan-1-ol gave a mixture of the *cis*- and *trans*-1 : 2 : 7 : 8 : 14 : 17-hexahydro-3 : 10-dimethoxychrysene. The major, higher-melting, and less soluble isomer * was assigned the *trans*-configuration (V) by analogy with the known properties of the *cis*- and *trans*-forms of 1 : 2 : 7 : 8 : 14 : 17-hexahydrochrysene [14] and 1 : 2 : 7 : 8 : 14 : 17-hexahydro-4 : 10-dimethoxychrysene [15] and by taking into account the known results of reducing 1 : 2 : 7 : 8-tetrahydro-4 : 10-dimethoxychrysene with the same reagent.[11] In the sequel this conclusion proved to be correct. The *trans*-isomer could be obtained in a satisfactory state of stereochemical purity by crystallisation of the reaction mixture under controlled conditions. Reduction of the tetrahydro-compound (IV) with potassium in *iso*propyl alcohol, or with sodium or lithium in liquid ammonia, was less satisfactory as regards both the total yield and stereochemical specificity. Reduction of the hexahydro-compound (V) with lithium (60 g.-atoms) and ethanol in liquid ammonia followed by treatment of the product with mineral acid gave an αβ-unsaturated ketone $C_{19}H_{22}O_2$ produced by reduction of one of the aromatic nuclei. It is known that 1 : 2 : 3 : 4-tetrahydro-6-methoxynaphthalene undergoes reduction with alkali metal and alcohol in liquid ammonia much more readily than the 5-methoxy-isomers,[16] and hence it was taken as

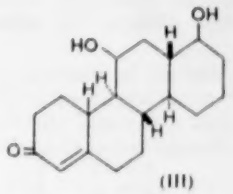
* We are informed by Dr. J. Walker that he and Dr. P. A. Robins have prepared this compound by an independent route which was reported at a meeting of the Chemical Society on February 16th, 1956.

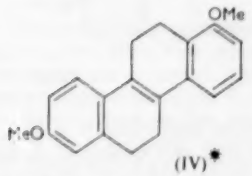
[8] *Chem. Eng. News*, 1956, **34**, 2134.
[9] Johnson, Lemaire, and Pappo, *J. Amer. Chem. Soc.*, 1953, **75**, 4866.
[10] Johnson, Bannister, Pappo, and Pike, *ibid.*, 1955, **77**, 817.
[11] Birch and Smith, *J.*, 1951, 1882.
[12] Birch and Quartey, *Chem. and Ind.*, 1953, 489.
[13] Johnson, Dehn, and Chinn, *J. Org. Chem.*, 1954, **19**, 670.
[14] Ramage and Robinson, *J.*, 1933, 607.
[15] Lewis, Ramage, and Robinson, *J.*, 1935, 1412; Wilds and Sulton, *J. Org. Chem.*, 1951, **16**, 1371.
[16] Birch, Murray, and Smith, *J.*, 1951, 1945.

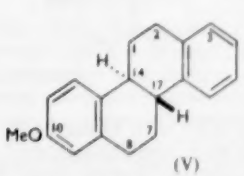
virtually certain that this ketone has the structure (VI) derived by reduction of the 1 : 2 : 4-substituted benzene ring. The light absorption supported this view. Although the position of the maximal ultraviolet absorption (233 mμ) is at a lower wavelength than would be predicted (244 mμ) on the basis of a modified version of Woodward's rules,[17] certain similarly substituted steroid ketones, *e.g.*, 3 : 12-dioxochol-4-enic acid [18] and 11-deoxy-17-hydroxycorticosterone [19] show deviations of this order. Reduction of the 1 : 2 : 3-substituted benzene ring could lead theoretically to two αβ-unsaturated ketones, (VII) and (VIII), resulting respectively from the 5 : 15- and 4 : 16-dihydro-derivatives. The former

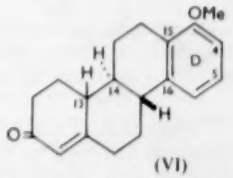

(I)


(II)


(III)


(IV)*


(V)


(VI)

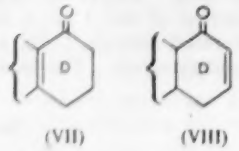
* This and other formulæ for (±)-compounds imply the presence of an equal amount of the enantiomer. For these formulæ, and the resulting names, the hydrogen atom attached to $C_{(9)}$ in the steroid skeleton ($C_{(14)}$ in the hydrochrysene skeleton) has arbitrarily been taken as in the α-configuration.

should absorb around 249 mμ, the latter around 227 mμ. The infrared absorption spectrum shows bands at 789, 742, and 712 cm.$^{-1}$ which are consistent with the presence of a 1 : 2 : 3-trisubstituted aromatic nuleus; [20] there is no strong band in the 860—800 cm.$^{-1}$ region and hence a 1 : 2 : 4-trisubstituted benzene ring such as would be present in (VII) or (VIII) is contraindicated.[21] These conclusions were later verified. The configuration of the hydrogen atom attached to $C_{(13)}$ is unknown but is established during a bond-migration reaction known to generate the thermodynamically most stable isomer.[11] Therefore the expectation is that the hydrogen atom at $C_{(13)}$ will be *trans* to that at $C_{(14)}$, *i.e.*, β as represented in (VI). In this connection it is relevant that rotational evidence as well as the high physiological activity is consistent with the assumption that the β-configuration obtains at $C_{(10)}$ (steroid numbering) in the 19-norhormones similarly formed by reduction of œstrone derivatives.[11,22]

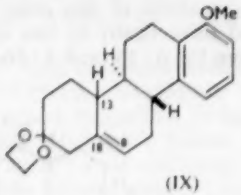
The reaction of the keto-ether (VI) with ethylene glycol in benzene in the presence of toluene-*p*-sulphonic acid proceeded normally. With αβ-unsaturated ketones dioxolan formation proceeds with a shift of the double bond to the βγ-position [23] which in the case of the substance (VI) can be either the 8(18)- or the 13(18)-position. The infrared absorption spectrum of the ketal which shows bands at 830 and 826 cm.$^{-1}$ is consistent with the

[17] Fieser and Fieser, "Natural Products Related to Phenanthrene," 3rd edn., Reinhold Publ. Corp., New York, 1949, p. 190.
[18] Sawlewicz and Reichstein, *Helv. Chim. Acta*, 1937, **20**, 949.
[19] Reichstein, *ibid.*, p. 953.
[20] Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, p. 66.
[21] Ref. 20, p. 67.
[22] Klyne, *J.*, 1952, 2916; Wilds and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 5366.
[23] Fernholz and Stavely, Abs. 102nd Meeting Amer. Chem. Soc., Atlantic City, N.J., 1941; 39M; Poos, Arth, Beyler, and Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 423.

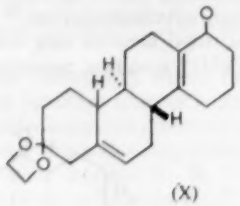
presence of a trisubstituted ethylenic centre [24] and therefore favours the structure (IX), although there is some evidence for inhomogeneity in the product. The point is of no practical importance here, however, since acid hydrolysis will generate the same αβ-unsaturated ketone.



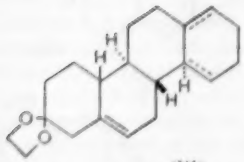
(VII) (VIII)



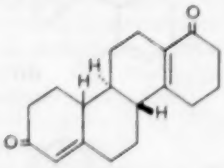
(IX)



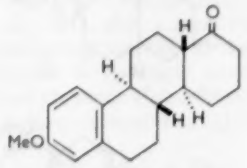
(X)



(XI)



(XII)



(XIII)

Reduction of the ketal-ether (IX) with lithium (300 g.-atoms) and ethanol in liquid ammonia followed by hydrolysis with aqueous-ethanolic oxalic acid and treatment of the product with aqueous-ethanolic sodium acetate gave, as the major product, an αβ-unsaturated ketone $C_{20}H_{26}O_2$, the ultraviolet absorption ($\lambda_{max.}$ 248·5 mμ) of which is in good agreement with that predicted for structure (X). A minor product, arising from the reductive removal of the 3-methoxy-group was a diene $C_{20}H_{28}O_2$, in which one double bond is presumably in the 8(18)-position, and the other forms part of ring D. As a point of theoretical interest, we have attempted to obtain further information about the position of this double bond by determining the ultraviolet absorption of the diene in the 200—220 mμ region. From the data given by Bladon, Henbest, and Wood [25] for steroid olefins it appears that the low ε values at 215—220 mμ (10—20) could not have resulted from the addition of the curves for a trisubstituted and tetrasubstituted olefinic centre, and so the 15(16)-position for the second double bond is excluded. The curve corresponds most closely to that produced by the addition of the curves for two trisubstituted olefinic centres, although the presence of a disubstituted double bond cannot with certainty be excluded. It rises smoothly from ε 1500 at 215 mμ through ε 7000 at 210 mμ and flattens to ε 10,000 at 200 mμ. The diene therefore probably has structure (XI).

Reduction of the ketone (X) with lithium and ethanol in liquid ammonia followed by treatment with hydrochloric acid gave a hydroxy-ketone, m. p. 215—218°, $\lambda_{max.}$ 240·5 mμ, which, on the basis of its infrared absorption spectrum and a mixed-melting-point determination, proved to be identical with the compound believed to be have structure (II; R = H) prepared by Johnson and his co-workers.[13] The sample of D-homo-18 : 19-bisnortestosterone prepared by Johnson was obtained from the intermediate (XIII) which has been converted into œstrone.[26] Hence the only elements in the structure (II) remaining unproved are the configurations of the hydrogen atom at $C_{(13)}$ and the 3-hydroxyl group. It is known that the reduction of carbon–carbon multiple-bond systems with dissolving metals in liquid ammonia usually affords the thermodynamically most stable isomer,[11,27] and on the basis of this rule it would be predicted that reduction of the ketone

[24] Ref. 20, p. 44.
[25] Bladon, Henbest, and Wood, *J.*, 1952, 2737.
[26] Johnson, Banerjee, Schneider, Gutsche, Shelberg, and Chinn, *J. Amer. Chem. Soc.*, 1952, **74**, 2832.
[27] Birch, *Quart. Rev.*, 1950, **4**, 69; Barton and Robinson, *J.*, 1954, 3045.

(X) should give a product having the asymmetric centres in the alternating *trans*-configurations and the 3-hydroxyl group in the β(equatorial)-configuration, and on acid hydrolysis the form (II) should result. Unpublished work has shown that, depending on the conditions, this rule need not be generally valid; it should however apply in this case.

Reduction of the ether (V) with lithium (250 g.-atoms) and ethanol in liquid ammonia and treatment of the product with hydrochloric acid gave a diketone (XII) whose structure follows from its identity with the product obtained by acid hydrolysis of keto-ketal (X). Further reduction of this diketone (XII) with lithium in liquid ammonia gave a saturated diketone which should be [27,28] the androstane-3 : 17-dione analogue (I; R = H). The same compound was obtained by reducing the unsaturated diketone (XII) with lithium and alcohol in liquid ammonia and oxidising the product in acetic acid solution with chromium trioxide.

Tests on the compounds (I; R = H), (II; R = H), and the propionate of the latter in capons showed no androgenic activity in doses up to 1 mg. Johnson, Dehn, and Chinn [13] showed that the compound (II; R = H) has no androgenic activity but has a high myotrophic activity. Compounds of this type may therefore prove to be useful anabolic agents. Further work is in progress.

Experimental

Evaporations were carried out under reduced pressure. Light petroleum means the fraction of b. p. 60—80° unless stated otherwise. M. p.s denoted (K) were determined on the Kofler block and are corrected. Absorption spectra were determined by Mr. F. Hastings under the general supervision of Dr. F. B. Strauss. Infrared spectra were determined for Nujol mulls.

trans-1 : 2 : 7 : 8 : 14 : 17-*Hexahydro*-3 : 10-*dimethoxychrysene* (V).—Sodium (9·5 g.) was added to a refluxing solution of 1 : 2 : 7 : 8-tetrahydro-3 : 10-dimethoxychrysene [1] (2 g.) in redistilled butan-1-ol (250 c.c.). After 30 min. sodium (6·5 g.) was added and the refluxing continued until dissolution was complete (1·5 hr.). On cooling, water (200 c.c.) was added and the mixture set aside in the refrigerator. After 48 hr. the precipitate was collected, washed thoroughly with water, dried, and recrystallised from ethanol to give the almost pure *trans*-hexahydrodimethoxychrysene as fine needles (0·81 g.), m. p. 127—130° (sintering at 123°). This preparation was used in all subsequent reductions. After recrystallisation from ethanol and then ethyl acetate it had m. p. 132·5—134·5°. A portion (300 mg.) in benzene was adsorbed on alumina (15 g.), and the column eluted with light petroleum and light petroleum containing increasing amounts of benzene. Light petroleum–benzene (9 : 1) eluted a fraction which, on recrystallisation from light petroleum–ethyl acetate, gave trans-1 : 2 : 7 : 8 : 14 : 17-*hexahydro*-3 : 10-*dimethoxychrysene* (V) as long fine needles, m. p. 133·5—134·5° unchanged on further crystallisation (Found: C, 81·6; H, 7·3. $C_{20}H_{22}O_2$ requires C, 81·6; H, 7·5%). Light absorption in EtOH: $\lambda_{max.}$ 273 (shoulder), 279, and 286 (shoulder) mμ (ε 3100, 3700, and 2100).

Ether (250 c.c.) was added to the mother-liquors after separation of the crude *trans*-compound and the organic layer was separated, dried, and evaporated to an oil which was dissolved in a little ether. Next day the deposited crystals were washed with ether and ethanol and recrystallised from ethanol to give the almost pure *cis*-hexahydrodimethoxychrysene as stout prisms (0·23 g.), m. p. 115·5—116·6°. Purification by chromatography as with the *trans*-isomer gave the cis-1 : 2 : 3 : 4 : 14 : 17-*hexahydro*-3 : 10-*dimethoxychrysene*, m. p. 119·5—120·5° unchanged on further recrystallisation and depressed on admixture with (V) (Found: C, 81·6; H, 7·5%). Light absorption in EtOH: $\lambda_{max.}$ 271 (shoulder), 279, and 287 (shoulder) mμ (ε 2400, 2900, and 1800). The oil (0·54 g.) from the ethereal mother-liquors gave with Brady's reagent a gummy 2 : 4-dinitrophenylhydrazone. The combined oils from a number of similar reductions were hydrolysed with hydrochloric acid in ethanol, and the product chromatographed on Florex. Benzene eluted a small quantity of a ketone, m. p. 208—211°, identical with 1 : 2 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-decahydro-3-methoxy-10-oxochrysene (below) (Found: C, 80·8; H, 7·8. Calc. for $C_{19}H_{22}O_2$: C, 80·6; H, 7·9%).

1 : 2 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-*Decahydro*-3-*methoxy*-10-*oxochrysene* (VI).—trans-1 : 2 : 7 : 8 : 14 : 17-Hexahydro-3 : 10-dimethoxychrysene (1 g.) in tetrahydrofuran (70 c.c.) was added with stirring to a solution of lithium (1·45 g.) in liquid ammonia (200 c.c.). Ethanol (18 c.c.) was added dropwise during 20 min. When the blue colour was discharged (5 min.) water (150 c.c.) was added and the mixture was extracted with ether (4 × 100 c.c.). The ether

[28] Barton, *Experientia*, 1950, **6**, 316, and subsequent papers; Johnson, *ibid.*, 1951, **7**, 315

solution was washed with water, dried, and evaporated in a stream of nitrogen to a gum which was dissolved in ethanol (75 c.c.)–6N-hydrochloric acid (18 c.c.) at 60°. The solution was refluxed under nitrogen for 45 min. Water (100 c.c.) was added to the cooled solution, and the mixture was extracted with ethyl acetate–ether (1 : 1; 4 × 50 c.c.). The extract was washed with water, dried, and evaporated to small bulk. The precipitate was recrystallised from ethyl acetate to give 1 : 2 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-*decahydro*-3-*methoxy*-10-*oxochrysene* (VI) as fluffy crystals (0·37 g.), m. p. 208—210°. The analytical sample had m. p. 211—212° (Found : C, 80·8; H, 7·8%). Light absorption in EtOH : $\lambda_{max.}$ 233, 271 (infl.) and 280 (ε 23,900, 2800, and 2300). Infrared absorption : bands at 1669, 1616, 1600, 1580, 789, 742, and 712 cm.$^{-1}$. The mother-liquors from the crude ketone (VI) contained an oil (0·36 g.) which was dissolved in light petroleum–benzene (1 : 1; 20 c.c.) and adsorbed on Florex (15 g.). The column was washed with light petroleum containing increasing proportions of benzene. Benzene (120 c.c.) and benzene–chloroform (4 : 1; 30 c.c.) eluted fractions which on recrystallisation from ethyl acetate gave a further quantity (0·13 g.) of compound (VI), m. p. 208—209°. Recrystallisation of mother-liquors gave a further crop (0·06 g.), m. p. 208—209°.

10-*Ethylenedioxy*-1 : 2 : 7 : 9 : 10 : 11 : 12 : 13 : 14α : 17β-*decahydro*-3-*methoxychrysene* (IX).—The above decahydromethoxyoxochrysene (0·58 g.) was refluxed in benzene (35 c.c.) with ethylene glycol (0·5 c.c.) and toluene-*p*-sulphonic acid (*ca.* 20 mg.) for 4·5 hr. under a Dean–Stark trap. The cooled solution was washed with saturated sodium hydrogen carbonate solution, then water, dried, and evaporated to a crystalline residue which was dissolved in benzene–light petroleum (1 : 3; 15 c.c.) and adsorbed on Florex (12 g.). The same solvent mixture eluted a series of fractions, with m. p.s varying from 115·5—117° to 124—128° (sintering at 120°), the infrared absorption spectra of which were almost identical. The combined fractions were recrystallised from light petroleum, to give 10-*ethylenedioxy*-1 : 2 : 7 : 9 : 10 : 11 : 12 : 13 : 14α : 17β-*decahydro*-3-*methoxychrysene* (IX) (0·45 g.), m. p. 115—118° (Found : C, 77·7; H, 8·1. $C_{21}H_{26}O_3$ requires C, 77·3; H, 8·0%). Infrared absorption : bands at 1597, 1580, 830, and 826 cm.$^{-1}$.

10-*Ethylenedioxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-*tetradecahydro*-3-*oxochrysene* (X).—The foregoing ethylenedioxydecahydromethoxychrysene (0·53 g.) in tetrahydrofuran (50 c.c.) was added with stirring to liquid ammonia (200 c.c.) containing lithium (4 g.) and ethanol (80 c.c.) was run in as quickly as possible. When the blue colour had been discharged (15 min.) water (150 c.c.) was added and the product obtained in the usual way. It was dissolved in ethanol (60 c.c.), and oxalic acid dihydrate (0·92 g.) in water (12 c.c.) was added. The solution was kept at 25° for 45 min. and an excess of saturated sodium hydrogen carbonate solution was added. The mixture was extracted with ether (4 × 75 c.c.), and the ethereal solution was washed with water, dried, and evaporated to a gum. The latter was dissolved in ethanol (40 c.c.), and fused sodium acetate (9 g.) in water (10 c.c.) was added and the solution refluxed under nitrogen for 1 hr. Water (100 c.c.) was added to the cooled solution, and the mixture thoroughly extracted with ether (4 × 75 c.c.). The gummy product was dissolved in light petroleum–benzene (3 : 1; 10 c.c.) and adsorbed on Florex (20 g.). The column was washed with light petroleum (120 c.c.). Elution with light petroleum–benzene (3 : 1; 100 c.c.) gave a fraction which was recrystallised from light petroleum (b. p. 40—60°), to give probably 10-*ethylenedioxy*-1 : 2 : 3 : 4 : 5 : 7 : 9 : 10 : 11 : 12 : 13 : 14α : 15 : 17β(or -1 : 2 : 4 : 5 : 6 : 7 : 9 : 10 : 11 : 12 : 13 : 14α : 16 : 17β)-*tetradecahydrochrysene* (XI) as needles (85 mg.), m. p. 120—122° (Found : C, 80·3; H, 9·2. $C_{20}H_{28}O_2$ requires C, 80·0; H, 9·3%). Infrared absorption : bands at 860 and 831 cm.$^{-1}$. Elution with light petroleum containing increasing proportions of benzene gave a series of oils. Elution with benzene (total 350 c.c.), benzene–ether (19 : 1; 75 c.c.), and benzene–ether (9 : 1; 50 c.c.) gave a series of nine fractions with m. p.s varying from 113—119° to 133—137·5°, the last six all being over 130°. The infrared absorption spectra of all nine fractions were almost identical. The combined fractions were recrystallised from ether at −10° to give 10-*ethylenedioxy*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 9 : 10 : 11 : 12 : 13 : 14α : 17β-*tetradecahydro*-3-*oxochrysene* (X) (0·143 g.), m. p. 132—136° (Found : C, 76·4; H, 8·5. $C_{20}H_{26}O_3$ requires C, 76·4; H, 8·3%). Light absorption in EtOH : $\lambda_{max.}$ 248·5 mμ (ε 12,500). Infrared absorption : bands at 1661, 1618, 829, and 816·5 cm.$^{-1}$.

The oxo-ketal (X) (60 mg.) was refluxed in ethanol (25 c.c.)–6N-hydrochloric acid (6 c.c.) under nitrogen for 45 min. The partially crystalline product was washed with ether and recrystallised from ethyl acetate to give 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-tetradecahydro-3 : 10-dioxochrysene (XII) (20 mg.), m. p. 147—150° undepressed by the sample prepared as below and possessing the same infrared absorption spectrum.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 15β : 16α : 17β-*Hexadecahydro*-3-*hydroxy*-10-*oxochrysene* (II; R = H).—The above oxo-ketal (X) (143 mg.) in tetrahydrofuran (15 c.c.) was added with stirring to a solution of lithium (250 mg.) in liquid ammonia (100 c.c.). After 3 min. ethanol (5 c.c.) was added dropwise during 15 min. After the blue colour was discharged (15 min.), water (80 c.c.) was added and the mixture extracted with chloroform. The product was dissolved in ethanol (25 c.c.) and refluxed under nitrogen with 6N-hydrochloric acid (6 c.c.) for 40 min. The product was washed with a little ether to give slightly yellow crystals (82 mg.) which were dissolved in benzene (15 c.c.) and adsorbed on Florex (6 g.). The column was first washed with benzene (70 c.c.). Further elution with benzene and benzene containing proportions of chloroform up to 50% eluted a series of crystalline fractions. The first two were rejected and the remainder recrystallised from benzene, to give the 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 15β : 16α : 17β-hexadecahydro-3-hydroxy-10-oxochrysene (II; R = H) as long needles (45 mg.), m. p. 208—213°(K) undepressed by the sample prepared by Johnson, Dehn, and Chinn,[18] and possessing the same infrared absorption spectrum (Found: C, 78·6; H, 9·55. Calc. for $C_{18}H_{26}O_2$: C, 78·8; H, 9·4%). Light absorption in ethanol: $\lambda_{max.}$ 240·5 mμ (ε 17·000) [Johnson and his co-workers give m. p. 211·5—213° and $\lambda_{max.}$ 240·5 (ε 17,000)]. Infrared absorption: bands at **3401**, **1650**, and **1631** cm.$^{-1}$. This compound, purified further by chromatography on deactivated alumina, gave a sample which after two further recrystallisations from benzene had m. p. 215—218°(K).

The *propionate* was obtained from light petroleum (b. p. 40—60°) as needles, m. p. 152—155°(K) (Found: C, 75·8; H, 8·95. $C_{21}H_{30}O_3$ requires C, 76·4; H, 9·1%). Infrared absorption: bands at **1733**, **1667**, **1618**, and **1187** cm.$^{-1}$.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-*Tetradecahydro*-3 : 10-*dioxochrysene* (XII).—The hexahydrodimethoxychrysene (V) (1 g.) in tetrahydrofuran (100 c.c.) was added with stirring to liquid ammonia (300 c.c.) containing lithium (6·2 g.). Ethanol (100 c.c.) was run in as quickly as possible and when the blue colour was discharged (30—60 min.) water (300 c.c.) was added and the mixture extracted with ether. The gum obtained by evaporating the ether solution in a stream of nitrogen was dissolved in ethanol (75 c.c.) and refluxed with 6N-hydrochloric acid (18 c.c.) under nitrogen for 45 min. Water (100 c.c.) was added to the cooled solution, and the mixture was extracted with ether–ethyl acetate (1 : 1; 4 × 50 c.c.). The product was dissolved in benzene–light petroleum (1 : 1; 20 c.c.) and adsorbed on Florex (30 g.). The column was eluted with the same solvent mixture, with light petroleum containing increasing amounts of benzene, benzene, and benzene containing increasing amounts of chloroform. Benzene–chloroform (1 : 1) and benzene–chloroform (1 : 3) gave fractions which on recrystallisation from ethyl acetate gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10 : 11 : 12 : 13 : 14α : 17β-*tetradecahydro*-3 : 10-*dioxochrysene* (XII) (110 mg.), m. p. 145—150°. A sample recrystallised for analysis had m. p. 149—150° (Found: C, 79·5; H, 8·5. $C_{18}H_{22}O_2$ requires C, 80·0; H, 8·15%). Light absorption in EtOH: $\lambda_{max.}$ 244·5 mμ (ε 25,500). Infrared absorption: bands at **1664** and **1626** cm.$^{-1}$.

1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 12 : 13β : 14α : 15β : 16α : 17β : 18α-*Octadecahydro*-3 : 10-*dioxochrysene*.—(*a*) The tetradecahydrodioxochrysene (XII) (272 mg.) in tetrahydrofuran (20 c.c.) was added with stirring to a solution of lithium (55 mg.) in liquid ammonia (50 c.c.). After 10 min. ammonium chloride was added to discharge the blue colour. The product was dissolved in benzene (25 c.c.) and adsorbed on Florex (10 g.). Benzene (125 c.c.) and benzene–chloroform (9 : 1; 25 c.c.) eluted fractions which on recrystallisation from ethyl acetate–light petroleum gave 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8 : 9 : 10 : 11 : 12 : 13β : 14α : 15β : 16α : 17β : 18α-*octadecahydro*-3 : 10-*dioxochrysene* (I; R = H) as slender needles (39 mg.), m. p. 156—157° (Found: C, 78·6; H, 9·6. $C_{18}H_{24}O_2$ requires C, 78·8; H, 9·5%). Infrared absorption: band at **1706** cm.$^{-1}$. Benzene–chloroform (9 : 1, 25 c.c.; 4 : 1, 50 c.c.; 3 : 2, 25 c.c.) eluted fractions which on recrystallisation from ethyl acetate gave a hydroxy-ketone, m. p. 200—203°, giving infrared absorption bands at **3367** and **1706** cm.$^{-1}$. Benzene–chloroform (3 : 2; 75 c.c.) next eluted a fraction which after recrystallisation from ethyl acetate had m. p. 257—259° and is probably a diol (infrared absorption band at **3247** cm.$^{-1}$).

In one experiment in which a sample of (XII) having m. p. 140—145° was used, benzene eluted first from Florex a small quantity of a *dione* obtained from light petroleum–ethyl acetate as needles, m. p. 167—168° depressed on admixture with (I; R = H) (Found: C, 79·0; H, 9·6. $C_{18}H_{24}O_2$ requires C, 78·8; H, 9·5%), with infrared absorption bands at **1721** and **1701** cm.$^{-1}$.

(*b*) The tetradecahydrodioxochrysene (XII) (110 mg.) in tetrahydrofuran (10 c.c.) was added with stirring to a solution of lithium (112 mg.) in liquid ammonia (100 c.c.). After 15 min., ethanol (4 c.c.) was added during 10 minutes, and when the blue colour was discharged water

(50 c.c.) was added and the product collected in chloroform. It was dissolved in acetic acid (3 c.c.), and a solution of chromium trioxide (82 mg.) in acetic acid (3·6 c.c.)–water (0·4 c.c.) was added. After 23 hr. at room temperature the mixture was worked up in the known manner, to give an oil which was dissolved in benzene (5 c.c.) and chromatographed on Florex (5 g.) as under (*a*), yielding the perhydrodioxochrysene (I; R = H) (25 mg.), m. p. 158—159° undepressed by the specimen as prepared as under (*a*).

We are grateful to the University of Oxford for a Pressed Steel Fellowship (H. S.), to the Upjohn Co., Kalamazoo, and to CIBA, Basle, for biological tests.

THE DYSON PERRINS LABORATORY, OXFORD.
CHEMISTRY DEPARTMENT, UNIVERSITY OF MANCHESTER. [*Received, July 23rd*, 1956.]

957. *Germanium Esters. Part I. Parachors and Molecular Structure.*

By D. C. BRADLEY, L. J. KAY, and W. WARDLAW.

The alkyl orthogermanates, $Ge(OR)_4$, where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, n-C_5H_{11}, and CMe_2Et, have been prepared either by reactions involving the tetrachloride and the appropriate alcohol in the presence of ammonia or by alcohol interchange. The latter method failed to produce $Ge(OBu^t)_4$ from $Ge(OEt)_4$ owing to steric hindrance. The densities and surface tensions of the germanium esters were accurately measured between 20° and 40° and molecular volumes and parachors were calculated. The parachors, analysed by Gibling's method, showed considerable deviations from additivity which were identified by conformational analysis with volume losses caused by overlap of van der Waals fields in the preferred conformations. Parachor data on normal alkyl orthocarbonates and orthosilicates were similarly considered.

THIS work was initiated to try to establish the structural behaviour of compounds having the molecular formula $M(OAlk)_4$, where M is a central atom linked tetrahedrally to oxygen. In particular, information on systems containing no major intermolecular bonding between metal and oxygen was required and compounds of carbon, silicon, and germanium appeared to satisfy this requirement. Germanium esters were chosen first because little is known of their physicochemical properties and secondly because we were able to prepare esters containing primary, secondary, or tertiary alkyl groups whereas the preparation of branched-chain orthocarbonates or orthosilicates is difficult owing to steric hindrance.

The esters $Ge(OR)_4$, where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, n-C_5H_{11}, and CMe_2Et, were prepared and their densities and surface tensions were measured over the range 20—40°. Their preparation either from the tetrachloride by the ammonia method or by alcohol interchange has been mentioned in a preliminary note [1] but we have since discovered that the *tert.*-butoxide cannot be obtained by interchange from the ethoxide, the reaction stopping at the formation of $Ge(OEt)(OBu^t)_3$ which is resistant to further interchange with *tert.*-butyl alcohol, undoubtedly for steric reasons.

TABLE 1.

R in $Ge(OR)_4$ ...	Me	Et	Pr^n	Pr^i	Bu^n	Bu^i	Bu^s	Bu^t *	n-C_5H_{11}	CMe_2Et
d_{25}	1·3244	1·1288	1·0565	1·0245	1·0167	1·0054	1·0164	1·0574	0·9941	1·0425
γ_{25}	22·49	23·23	23·61	20·76	24·00	23·25	23·47	22·74	24·18	23·39
V_{25}	148·5	224·0	292·5	301·6	358·9	363·1	359·1	345·2	423·8	404·0
$[P]$	323·7	491·9	644·7	643·9	794·6	797·4	790·0	754·5	939·4	888·0
$[P]/V_{25}$	2·18	2·20	2·20	2·13	2·21	2·20	2·20	2·19	2·22	2·20

* M. p. 23·5°.

The densities and the surface tensions of each compound were linear functions of temperature whilst the parachor was independent of temperature. The densities (g./c.c.), molar volumes (c.c.), and surface tensions (dynes/cm.) at 25° together with the mean parachors $[P]$ and the ratio parachor : molar volume (at 25°) are presented in Table 1.

[1] Bradley, Kay, and Wardlaw, *Chem. and Ind.*, 1953, 746.

The Eötvös constant, $k = -d(\gamma V^{2/3})/dT$, was independent of temperature for each compound and suggests that these liquids are unassociated. With regard to the *n*-alkyl orthogermanates, the expected decrease in density and increase in molar volume and parachor with increasing length of alkyl chain is evident in Table 1. The surface tension increases steadily with length of alkyl chain. The isomeric butyl esters form an exceptional group and it is noteworthy that the *iso*butyl derivative has the maximum molar volume and parachor. Moreover, although the surface tension of the *iso*propyl ester is lower than that of the *n*-propyl ester and the *tert.*-amyl ester has a lower value than the *n*-pentyl, there is not a steady change of surface tension with degree of branching in the butyl esters. It appears that some unusual structural factors are brought into operation in passing from the *n*-butyl to the *tert.*-butyl ester. Another feature of Table 1 is the constancy of the ratio $[P]/V_{25}$ since only the *iso*propyl ester differs appreciably from the average value of 2·19.

Although the early enthusiasm for Sugden's parachor diminished later there are signs [2] of renewed interest in this method of comparing molar volumes under standard conditions of intermolecular forces. In particular, Gibling's recent work [3] has shown the potentialities of the parachor as a means of revealing structural abnormalities in liquids. He suggests that the parachor value for an atom is affected by (i) the nature of other atoms bonded to it and (ii) interference from non-bonded neighbouring atoms, and instead of atomic parachors he uses group parachors; he successfully applied this method to a large number of compounds. Although we do not necessarily accept all of Gibling's postulates, in particular the view that interaction involving hydrogen atoms on hydrocarbons can be neglected, the fundamental idea of the group parachor seems reasonable and we have applied Gibling's method to the germanium esters. The following group of reduced parachors [4] were used: $CH_3(C) = CH_3(O) = 55{\cdot}2$; $(C)CH_2(C) = 39{\cdot}8$; $(C)CH_2(O) = 39{\cdot}3$; $(C)_2CH(C) = 22{\cdot}2$; $(C)_2CH(O) = 21{\cdot}2$; $(C)_2C(C)_2 = 2{\cdot}4$ and $(C)_3C(O) = 0{\cdot}9$. The parachor of each germanium ester was used to determine the reduced parachor (R.P.) of the central group of germanium and four oxygen atoms, *i.e.*, R.P. $Ge[O(C)]_4$. First, the reduced parachor of the ester was calculated by subtracting from the parachor $[P]$ the value of the expansion correction (E.C.) obtained by interpolation from Gibling's table.[4] Then a summation of the group parachors of $CH_3(C)$, $(C)CH_2(C)$, etc., was made to give the reduced parachor of alkyl groups ($\sum$R.P. alkyl) which was then subtracted from the reduced parachor of the ester to give R.P. $Ge[O(C)]_4$. The relevant values are presented in Table 2.

TABLE 2.

R in $Ge(OR)_4$	E.C.	R.P. Ester	$\sum$R.P. Alkyl	R.P. $Ge[O(C)]_4$	Δ	Δ'
Me	1·0	322·7	220·8	101·9	11·5	—
Et	2·3	489·6	378·0	111·6	1·8	—
Pr^n	4·1	640·6	537·2	103·4	10·0	8·2
Pr^i	4·1	639·8	526·4	113·4	0	—
Bu^n	6·3	788·3	696·4	91·9	21·5	11·5
Bu^i	6·4	791·0	687·6	103·4	10·0	—
Bu^s	6·3	783·7	685·6	98·1	15·3	—
Bu^t	5·6	748·9	666·0	82·9	30·5	—
n-C_5H_{11}	8·7	930·7	855·6	75·1	38·3	16·8
CMe_2Et	7·8	880·2	825·2	55·0	58·4	—

Ideally the value of R.P. $Ge[O(C)]_4$ should be constant irrespective of the ester and the remarkable variation shown in Table 2 suggests the presence of structural abnormalities associated with alkyl groups. Before interpreting these results it is convenient to give the values for R.P. $C[O(C)]_4$ and R.P. $Si[O(C)]_4$ which we have calculated from the parachor data for *n*-alkyl orthocarbonates and orthosilicates published by Arbusov and Vinogradova.[5] The values are given in Table 3 which also contains values for Δ, the

[2] Mumford and Phillips, *J.*, 1929, 2112; Vogel *et al.*, *ibid.*, 1943, 333, 363; 1946, 143; 1948, 624; Quayle, *Chem. Rev.*, 1953, **53**, 439; Edward, *Chem. and Ind.*, 1956, 774.
[3] Gibling, *J.*, 1941, 298, 304; 1942, 661, 665; 1943, 146; 1944, 380, 383; 1945, 236.
[4] Gibling, "Molecular Volume and Structure," unbound M.S. presented to Library of Chemical Society, May, 1956.
[5] Arbusov and Vinogradova, *Doklady Akad. Nauk S.S.S.R.*, 1948, **60**, 799.

difference between R.P. $M[O(C)]_4$ for the methyl ester and any other ester, and Δ', which is the increment in ascending the homologous series $M(OC_nH_{2n+1})_4$.

The parachor for the *n*-pentyl orthosilicate was deduced by interpolation from the plot of parachor against number of carbon atoms in the alkyl group for the other esters. The values of Δ in Table 3 show a steady increase with increasing length of alkyl chain and Gibling [4] has previously pointed out a similar behaviour in the case of *n*-alkyl esters of dialkyl carbonates, sulphates, sulphites, phosphates, and phosphites. He attributed this to parallelism of the alkyl chains, and Arbusov and Vinogradova [5] appear to have applied

TABLE 3.

R in $C(OR)_4$	R.P. $C[O(C)]_4$	Δ	Δ'	R in $Si(OR)_4$	R.P. $Si[O(C)]_4$	Δ	Δ'	R in $Si(OR)_4$	R.P. $Si[O(C)]_4$	Δ	Δ'
Me	77·3	0	—	Me	106·2	0	—	*n*-C_6H_{13}	86·8	19·4	3·6
Et	76·2	1·1	1·1	Et	105·0	1·2	1·2	*n*-C_7H_{15}	83·4	22·8	3·4
Pr^n	71·8	5·5	4·4	Pr^n	98·7	7·5	6·3	*n*-C_8H_{17}	81·2	25·0	2·2
Bu^n ...	66·8	10·5	5·0	Bu^n	96·4	9·8	2·3	*n*-C_9H_{19}	74·1	32·1	7·1
				n-C_5H_{11}	90·4	15·8	6·0	*n*-$C_{10}H_{21}$	73·0	33·2	1·1

Gibling's method and interpretation to the orthocarbonates and orthosilicates. It is noteworthy that in the dialkyl ethers the only anomaly found by Gibling [4] was a small reduction in parachor with the *n*-butyl groups which was interpreted as a bending back of the alkyl chain bringing the δ-carbon atom closer to the oxygen. It appears that the " parallelism " of *n*-alkyl chains occurs when they are linked by oxygen to another central atom, as in the ortho-esters, but not when linked to the same oxygen atom, presumably because in the latter case the zig-zag conformation of hydrocarbons is still maintained, *viz.*, (I). Returning to our results in Table 2, it is interesting to note that with the exception of the methyl ester, which is clearly anomalous, the *n*-alkyl germanates show a progressive reduction in R.P. $Ge[O(C)]_4$ with increase in number of carbon atoms in the alkyl chain {the values of Δ are relative to zero for the *iso*propyl ester which has the maximum value for R.P. $Ge[O(C)]_4$}. This behaviour is similar to that of the orthocarbonates and orthosilicates, but it is extremely interesting that in the isomeric butyl germanates reductions also occur in the order $Bu^s > Bu^n > Bu^n > Bu^i$ with branching of the alkyl group. Moreover, the reduction for the *tert.*-amyl ester is considerably greater than for the *n*-pentyl ester. On the other hand, the *iso*propyl ester (arbitrarily taken as $\Delta = 0$) has a smaller reduction than the *n*-propyl ester. Therefore it is clear that branching of the alkyl chain prevents the parallelism found in *n*-alkyl derivatives, but that extensive branching leads to another type of parachor reduction. With regard to methyl orthogermanate we suggest that this has an anomalous parachor because it gives a value for R.P. $Ge[O(C)]_4$ which is smaller than the corresponding value for $Si[O(C)]_4$ when, from a consideration of atomic radii, it should be greater. Two explanations are possible. Either the methyl orthogermanate molecules are able to pack more closely in the liquid state by virtue of being smaller and more nearly spherical than the higher esters or there may be some intermolecular association involving germanium and oxygen.

The enormous parachor reductions for the *tert.*-butyl and *tert.*-amyl esters prompted us to set up atomic models for germanium esters. The following bond lengths were used : C–C = 1·54 Å, C–O = 1·43 Å, and Ge–O = 1·72 Å, the last value being derived by application of the electronegativity correction [6] to the sum of the covalent atomic radii (Ge = 1·22 Å, O = 0·66 Å). It was further assumed that the angles $\angle$OGeO, $\angle$GeOC, and $\angle$OCC were all tetrahedral. These models showed clearly that in the highly branched esters rotation of alkoxide groups was severely restricted and that for all conformations of each molecule there was considerable overlap of the van der Waals volumes of the atoms. Accordingly we have attempted to measure the decrease in volume due to this overlap by measuring interatomic distances in these models in conformations of minimum intramolecular congestion. Using the van der Waals radii CH_3 = 2·0 Å, O = 1·4 Å, and Ge = 2·02 Å, we then calculated the volume of the two spherical caps produced by intersection of the van der Waals spheres of interacting atoms or groups and this gave the

[4] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1945, p. 81.

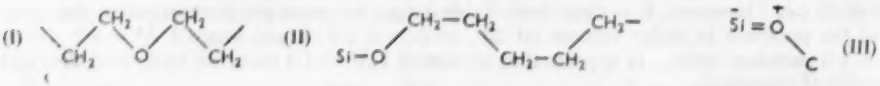
volume (in Å³) lost by overlap or interference of non-bonded atoms. An approximate relation between volume in Å³ and parachor units was derived as follows. Gibling [4] has calculated the reduced parachor of methane to be 68·4 units. If it be assumed that methane consists of a hexagonal close-packed array of molecules of radius 2·0 Å then the volume occupied by a molecule is $5{\cdot}66 \times 2{\cdot}0^3 = 45{\cdot}3$ Å³ ≡ 68·4 parachor units, whence 1 Å³ ≡ 1·5 parachor units. Alternatively we may choose an imaginary germanium ester molecule occupying a volume = 1 Å³ = 10^{-24} c.c. at 25°. Then 1 mole would occupy 0·6025 c.c. However, it is clear from Table 1 that for most germanium esters the ratio of the parachor to molar volume (at 25°, in c.c.) is 2·2 : 1 and hence 1 Å³ = $2{\cdot}2 \times 0{\cdot}60$ = 1·3 parachor units. It appears that a value of 1 Å³ ≡ 1·4 parachor units is of the right order of magnitude.

Methyl Esters.—Inspection of models shows that rotation of alkoxide groups around the oxygen–central atom bond is restricted even in the methyl esters and especially for methyl orthocarbonate. For example, the conformation having the maximum separation of methyl groups from neighbouring alkoxide oxygen atoms on the same molecule is the one with the methyl group staggered with respect to two neighbouring oxygen atoms. The interatomic distances between carbon and oxygen are then : orthocarbonate, 2·75 Å; orthosilicate, 3·0 Å; and orthogermanate, 3·14 Å; all these are considerably less than the sum of the van der Waals radii of oxygen and the methyl group (3·4 Å). Moreover each methyl group interacts with two others since the intercarbon distance (*ca.* 3·5 Å) is less than the van der Waals distance (4·0 Å). Further interaction occurs between methyl groups and the central atom and it is clear that considerable " loss of volume " occurs in the methyl esters. The total loss of volume will not differ greatly between the staggered or the eclipsed methyl . . . oxygen conformations because the smaller specific loss involved in the former is offset by the existence of twice as many interactions as in the latter. Thus the calculated total volume losses in the methyl orthocarbonate are : staggered Me . . . O, 3·1 Å³; eclipsed Me . . . O, 4·4 Å³. For methyl orthogermanate the corresponding values are 0·59 Å³ and 0·73 Å³ and similar values would be expected for methyl orthosilicate. However, these values are automatically included in the values of R.P. $C[O(C)]_4$ and R.P. $Si[O(C)]_4$ and will not affect values of Δ in Table 3.

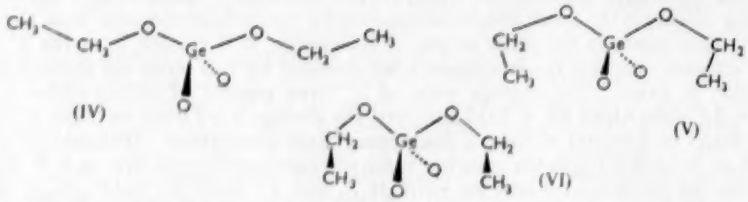
Normal Alkyl Esters.—Inspection of the increments Δ′ in Tables 2 and 3 reveals some interesting differences between the *n*-alkyl ortho-carbonates, -silicates, and -germanates. A striking feature is the much greater increments for the orthogermanates than the corresponding increments in the other series. Furthermore, it is evident from the Δ′ values for the orthosilicates that the increment is not constant for this series but shows a distinct alternation in value. The average value of Δ′ (even number of carbon atoms in alkyl group) is 2·1 units whilst for Δ′ (odd numbers) the average is 5·7 units and only in the step from *n*-hexyl to *n*-heptyl is there a discrepancy from alternation. It should be pointed out that an error of 0·1% in the parachor value will correspond to an error in R.P. $Si[O(C)]_4$ of 0·5 unit for $Si(OEt)_4$, 1·0 unit for $Si(OC_6H_{13})_4$ and 1·7 units for $Si(OC_{10}H_{21})_4$, so that the alternation in Δ′ values is significant compared with probable experimental error. On the other hand the values of Δ′ for the *n*-alkyl orthocarbonates and orthogermanates show a continuous increase in the increment with length of alkyl chain. Arbusov and Shavsa [7] have deduced from dipole-moment measurements that the rotation of the alkoxide groups is much more restricted in the orthocarbonates than in the orthosilicates whilst Moore, Gibbs, and Eyring [8] suggest that the straight-chain hydrocarbons up to $C_{10}H_{22}$ are essentially in the zig-zag conformation and rotating about the long axis above about room temperature. It seems likely that the restricted rotation in the orthocarbonates causes the alkyl chains to radiate from the central CO_4 group as zig-zag methylene chains sweeping out a smaller volume than the same number of methylene groups in the freely rotating hydrocarbons. This arrangement should lead to considerable intermolecular entanglement as the chain length increases. In the *n*-alkyl orthosilicates the alkyl chains are rotating more freely than in the orthocarbonates but the alternation in Δ′ values suggests that a sinusoidal conformation (II) tends to occur. In this model the methyl groups in

[7] Arbusov and Shavsa, *Doklady Akad. Nauk S.S.S.R.*, 1948, **69**, 599.
[8] Moore, Gibbs, and Eyring, *J. Phys. Chem.*, 1953, **57**, 172.

the *n*-propyl silicate come close to the oxygen atoms (the carbon–oxygen distance is 2·5 Å) causing a volume loss for four chains of 2·4 Å^3 = 3·4 parachor units whilst in the longer chains there will be extra volume losses in the odd-numbered chains owing to the proximity of the carbon atoms (C . . . C, 2·75 Å). The maximum contraction for four groups at each odd-number chain due to the latter effect would be *ca.* 5·4 Å^3 = 7·6 parachor units. An additional factor for the orthosilicates is the partial double-bond character in Si–O bonds



due to overlap of a lone electron pair in an oxygen p_π orbital with a vacant d_π orbital of the silicon. This will tend to increase the ∠SiOC angle from the assumed tetrahedral value towards 120° required for sp^2 hybrid bonds between oxygen and its adjacent atoms in (III) and it will impose an added barrier to rotation about the Si–O bond. In fact, Yamazaki [9] has deduced from electron-diffraction studies on methyl orthosilicate that rotation is restricted and the ∠SiOC angle is widened to 113°. This widening will ease the congestion of alkyl groups for the lower alkyl chains and it is possible for reasons not immediately obvious that the partial double bonding is the cause of the alternation effect apparent in the Δ′ values for the orthosilicates. This is consistent with the lack of alternation in the orthocarbonates and orthogermanates because Gordy's [10] deductions from nuclear quadrupole coupling constants for the tetrahalides suggest that double-bonding tendencies are in the order Si > Ge > C. In addition to the sinusoidal tendency of the alkyl chains in alkyl orthosilicates there is the possibility of parallelism of pairs of chains as suggested by Arbusov and Shavsa [7] but in view of the small values of Δ′ compared with those for the germanates it appears that parallelism is much less marked in *n*-alkyl orthosilicates than in *n*-alkyl orthogermanates. Our interpretation of the steadily increasing values of Δ′ for the orthogermanates is that these molecules prefer a conformation in which the alkyl chains are aligned parallel in two pairs disposed in planes approximately at right angles giving an elongated molecule. In building the ethyl orthogermanate molecule from the methyl derivative it is clear that the preferred conformation (IV) of the terminal



methyl group is transoid to the Ge–O–CH_2 system as shown (two Et groups omitted). The only additional volume loss in (IV) over that for the methoxide is a contribution caused by restricted rotation of the methyl group. Restricted rotation is severe because in conformation (V), with Ge·O·CH_2·CH_3 in a plane bisecting the line between the nearest two oxygen atoms the distance between methyl and oxygen is 2·66 and between methyl and germanium 2·46 Å. In conformation (VI) the distances are CH_3 . . . O, 1·86 and CH_3 . . . Ge, 3·0 Å. The total volume losses per molecule would be: (V), *ca.* 13·4 Å^3; (VI), *ca.* 11·8 Å^3. It is difficult to assess the volume loss in (IV) but if the methyl groups are " frozen " in this conformation, a loss of 5·8 Å^3 is estimated as follows. In a zig-zag polymethylene chain the maximum width of chain is 4·89 Å (including van der Waals radii) whilst the minimum width is 4·0 Å. The increment of length along the long axis due to each methylene group is 1·273 Å, hence for a normal hydrocarbon molecule rotating about the long axis a cylindrical volume is swept out and if the cylinders assume closest

[9] Yamazaki, Kotera, Yokoi, and Ueda, *J. Chem. Phys.*, 1950, **18**, 1414.
[10] Gordy, *Discuss. Faraday Soc.*, 1955, **19**, 27.

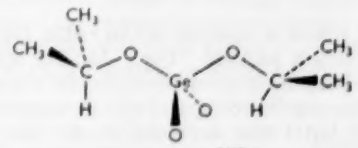
packing the volume per methylene group is $0{\cdot}866 \times 4{\cdot}89^2 \times 1{\cdot}273$ Å^3. When rotation about the long axis is completely restricted and the molecules take up simple cubic packing the volume per methylene group is $4{\cdot}89 \times 4{\cdot}0 \times 1{\cdot}273$ Å^3 and the loss in volume due to the restriction is thus 1·45 Å^3 per methylene group. Hence the major source of volume loss in the *n*-alkyl germanates, if they exist with the alkyl chains in two pairs of parallel zig-zags, will be due to the loss of rotation of these chains relative to free rotation in the hydrocarbons. This would require a volume loss of 5·8 Å^3 ≡ 8·1 parachor units in passing from one homologue to the next whereas Δ′ in Table 2 is not constant. This is not surprising because it is obvious from models that the chances of forming parallel chains increase steadily with length of chain. The values of Δ (Table 2) suggest that in the *n*-pentyl ester the chains are in fact close to parallelism since the difference in Δ between *n*-pentyl and ethyl is 36·5 units whereas a value of 32·3 units is calculated by assuming about half rotation of ethyl groups and no rotation of *n*-pentyl groups. Reasonable agreement is also found between experimental and calculated molecular volumes. In one case we have calculated the volume $V_1 = l \times 4{\cdot}9 \times 8{\cdot}0$ Å^3 of a parallelepiped formed by a non-rotating double-chain molecule of height 4·9 Å (for zig-zag polymethylene chain) and width 8·0 Å (for two parallel chains). The length l was measured from models and includes the van der Waals radii of the terminal methyl groups. This model neglects the constriction in the middle of the molecule caused by the GeO_4 grouping. In the second case we assume that the GeO_4 and α-methylene groups form a central box of volume $4{\cdot}78^2 \times 3{\cdot}92 = 89{\cdot}6$ Å^3 to which is added the volume $(2{\cdot}54n' + 4{\cdot}0) \times 8{\cdot}0 \times 4{\cdot}9$ Å^3 to give V_2 where $n' = 1, 2, 3$, and 4 for Me, Pr^n, Bu^n, and *n*-C_5H_{11}. The results are shown in Table 4; V is the experimental molecular volume (at 25°).

TABLE 4.

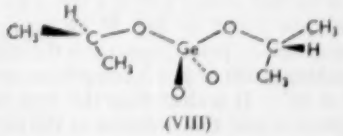
R in $Ge(OR)_4$	n'	l (Å)	V_1 (Å^3)	V_2 (Å^3)	V (Å^3)
Et	1	10·46	410·1	346·0	372·0
Pr^n	2	13·00	509·6	445·6	485·4
Bu^n	3	15·54	609·1	545·1	596·0
n-C_5H_{11}	4	18·08	708·8	644·6	703·0

In all cases the experimental values are between V_1 and V_2 and support the theory that the *n*-alkyl germanates assume the non-rotating parallel double-chain conformation as deduced from parachor data. An interesting consequence of this double-chain conformation is that intermolecular entanglement will be minimised, whereas in the orthocarbonates and orthosilicates this effect should be more pronounced. We have already suggested that this entanglement of alkyl chains is responsible for the anomalous entropies of vaporisation of *n*-alkyl orthosilicates [11] and it will be interesting to obtain similar data for the alkyl orthogermanates.

Branched-chain Esters.—Inspection of molecular models shows that (VII) is the conformation having least intramolecular congestion in the molecule of *iso*propyl orthogermanate (two Pr^i groups omitted). In conformation (VII) there is no interference between methyl



(VII)

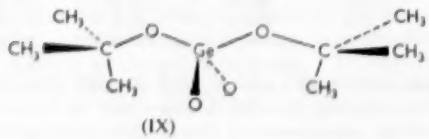


(VIII)

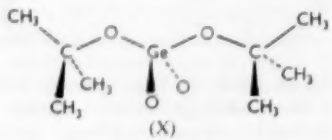
groups and oxygen whilst there are four methyl–methyl interactions (C . . . C = 3·25 Å) giving a volume loss of 2·16 Å^3 and eight methyl–CH interactions (C . . . C = 3·5 Å) with a loss of 1·92 Å^3 giving a total loss of *ca.* 4·1 Å^3 ≡ 5·7 parachor units greater than in the methyl ester. Rotation of the *iso*propyl group to give conformation (VIII) introduces considerable interaction especially between germanium and the *cis*-methyl groups with a

[11] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.

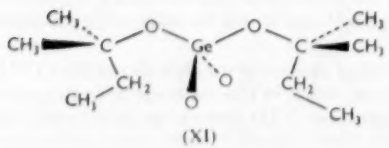
total volume loss of 15·7 Å^3 = 22 parachor units greater than in the methyl ester and it is obvious that conformation (VII) is preferred. It is interesting that the ethyl ester in conformation (IV) with half rotation of ethyl groups has a parachor reduction of 8·1 units which is 2·4 units greater than that of conformation (VII) for the *iso*propyl ester, in reasonable agreement with the experimentally deduced difference of 1·8 units (Table 2). Consideration of the models for the *tert.*-butyl ester shows that considerable intramolecular congestion is inevitable and is a minimum in conformation (IX) (two Bu^t groups omitted). This gives a disc-like molecule with eight "lateral" and four "lineal" methyl groups and the major volume loss occurs from interactions between oxygen and "lineal" methyls (O . . . C = 2·66 Å; volume loss 3·28 Å^3) and between lineal methyl groups and germanium (C . . . Ge = 2·46 Å; volume loss 8·97 Å^3). Additional smaller losses are caused by interaction between "lateral" methyl groups themselves, between "lateral" and "lineal" methyl groups, between tertiary carbon and "lateral" methyl groups and between tertiary carbon and "lineal" methyl groups giving a total volume loss of 19·5 Å^3 = 27·3 parachor units greater than in the methyl ester. In conformation (X) the volume loss has increased to 41 Å^3 = 57·4 parachor units and it is clear that the slightest rotation of either *tert.*-butyl or *tert.*-butoxide groups in conformation (IX) leads to a large decrease in effective volume. In fact the difference between the parachor losses of the *iso*propyl and *tert.*-butyl esters calculated on conformations (VII) and (IX) is 21·6 units compared with $\Delta' = 30{\cdot}5$ from Table 2. This higher value of Δ' may be due to oscillations of the alkyl groups which would cause a greater difference in parachor reductions, but alternatively the approximations involved in our calculations could account for the discrepancy. In either case it seems clear that the surprising parachor reduction in the *tert.*-butyl ester is closely related to the volume loss caused by interaction of the van der Waals fields of several of the atoms. The radial distance from the germanium atom to a "lateral" methyl group in conformation (IX) is *ca.* 5·5 Å (including van der Waals



(IX)



(X)



(XI)

radius of methyl group) and in a freely rotating spherical molecule of this radius the molecular volume would be 942 Å^3 for hexagonal closest packing. For a disc-like molecule rotating about the polar (lineal) axis through the germanium atom, the molecular volume for close packing is 650 Å^3 (6·2 Å being taken as thickness of disc) compared with the experimental 573 Å^3 at 25°. It is clear from this that the *tert.*-butyl ester molecules are disc-like rather than spherical and that rotation of the molecule is severely restricted, although it must be remembered that the experimental molecular volume at 25° is close to the value at the m. p. (23·5°). Inspection of molecular models also confirms the further parachor reduction in passing from the *tert.*-butyl to the *tert.*-amyl ester. If the extra methylene groups are interposed at the "lineal" methyl positions in conformation (IX) of the *tert.*-butoxide, then the methyl groups must take up positions remote from the germanium atom as in (XI). Rotation of the "ethyl"-methyl group around the "lineal" carbon–carbon bond is restricted by the oxygen and germanium atoms and neighbouring "lateral" methyl

groups. Hence the methyl group is more or less frozen and this will cause a volume loss of *ca.* 5·8 Å^3 plus the loss of 8·8 Å^3 due to interaction of the " ethyl "-methyl group in the staggered position to the two " lateral " methyl groups, giving a total additional loss in parachor of *ca.* 20·4 units compared with the difference of 28·4 units between the R.P. $Ge[O(C)]_4$ values for *tert.*-amyl and *tert.*-butyl esters. Similar reductions are calculated when the " ethyl " methylene group is placed at a " lateral " position instead of " lineal " in conformation (IX) or in any alternative position in conformation (X) of the *tert.*-butyl ester.

It is also clear why the Δ values for the isomeric butyl orthogermanates are in the peculiar order $Bu^s > Bu^s > Bu^n > Bu^i$. Thus for the normal isomer the value of Δ (21·5) is near to that calculated for fixed parallel pairs of butyl chains (26·7 units). On the other hand the *iso*butyl derivative (Δ = 10·0) may be considered as built up from the *n*-propyl ester (Δ = 10·0) by adding a methyl group at the 2-position in the *n*-propyl chain without causing any further volume loss. The *sec.*-butyl ester is especially interesting because it appears that optical isomerism in the *sec.*-butoxide group will have an effect on the steric interactions in the *sec.*-butyl germanate. Let us consider the *sec.*-butyl ester as built up by addition of a methyl group to a " lateral " methyl in conformation (VII) of the *iso*propyl ester. If all the *sec.*-butoxide groups are optically of one sign, then however these groups are rotated into conformation (VII) the " ethyl "-methyl groups always clash in pairs. The interaction is minimised when the " ethyl "-methyl groups are nearly *cis* to the alcohol hydrogen and are equidistant (3·5 Å) from a neighbouring " ethyl "-methyl group, a neighbouring " lateral " methylene group and the " lateral " methyl of the same *iso*propyl group. This gives a loss in volume of 5·8 Å^3 to which should be added *ca.* 5·8 Å^3 for restricted rotation of the ethyl groups (as in *tert.*-amyl ester) to make a total of 11·6 Å^3 ≡ 16·2 parachor units of further volume loss compared with the *iso*propyl ester. On the other hand by bending back these ethyl groups the conformation becomes that of the *n*-propyl ester with parallel *n*-propyl chains with methyl substitution at the alcohol carbon atom. The 1-methyl groups interact with one another in two pairs, and with the germanium atom and the alcohol carbon atoms to give a volume loss 3·5 Å^3 ≡ 4·9 parachor units in addition to that of the *n*-propyl ester (10·0) to make a resultant Δ = 14·9 parachor units. The *sec.*-butyl ester used in our work will be a mixture of diastereoisomers with regard to optical sign of the *sec.*-butoxide group but it is interesting that a molecule containing two groups of one sign and two of the opposite sign can assume a conformation based on (VII) in which there is no interaction between " ethyl "-methyl groups and having Δ = 14·3 parachor units. There is another conformation for this molecule having interaction between one pair of " ethyl "-methyl groups which would require a calculated Δ = 15·2 which is near our observed Δ = 15·3 units. On the other hand this molecule cannot assume the parallel chain conformation of the *n*-propyl ester because the 1-methyl groups interfere. It seems possible that different diastereoisomers of the *sec.*-butyl ester might differ in their values of Δ by something of the order of one parachor unit. We intend to test this point experimentally.

Although it cannot be claimed that our analysis of the parachor data has completely elucidated the preferred conformations of these ortho-esters, we feel that this work demonstrates the value of the parachor as a means of interpreting molecular structure especially when Gibling's method of group parachors is applied.

Experimental

Determination of Germanium.—The accurate analysis of germanium presents some difficulties; the problem has been reviewed.[12] In the present work four methods were used and each compound was analysed by at least two of them.

Gravimetric methods. (*a*) The sample (0·05—0·1 g.) was weighed into a prepared silica crucible and hydrolysed with aqueous ammonia (*d*, 0·88; 3 c.c.) and alcohol (1 c.c.). Careful evaporation (under the infrared lamp) of the solution to dryness was followed by ignition (900°)

[12] Kay, Ph.D. Thesis, London, 1955, 77.

and weighing as GeO_2. This method is only suitable for germanium esters which are chloride-free. (*b*) When chloride was present the germanium was precipitated from dilute sulphuric acid solution as the tannin complex by Holness's procedure.[13] The precipitate must be ignited to GeO_2 very carefully to avoid reduction of the germanium oxide by carbon.

Volumetric methods. (*a*) The sample (0·05—0·1 g.) was dissolved (the higher alkoxides required heating) in a freshly prepared aqueous solution of mannitol (5 g. in water, 20 c.c.) containing alcohol (1 c.c.). The solution was transferred to a potentiometric titration apparatus and the mannitol–germanic acid complex was titrated with sodium hydroxide (0·1—0·01N) with use of a glass electrode–calomel electrode cell. About 3 min. were allowed after each addition of alkali before the potential was measured and a small correction was applied for the acidity of the mannitol. Cluley's method [14] using an indicator did not give reproducible results.

(*b*) As an alternative to (*a*), the mannitol–germanic acid complex was titrated conductometrically with lithium hydroxide solution (*ca.* 0·05N), the end-point being deduced graphically. An advantage of this method was that chloride present could be detected and estimated on the same sample because two distinct end-points were detected.

Preparation of Alkyl Orthogermanates.—As germanium esters are readily hydrolysed, the same precautions were taken in drying apparatus and chemicals as described elsewhere.[15] Germanium tetrachloride [commercial (As <0·1 p.p.m.)] was used without further purification.

(a) *Preparation from the tetrachloride.* The alcohol and tetrachloride were dissolved in benzene (*ca.* 150 c.c.) and ammonia was passed in. Although a white cloud then appeared in the vapour space no precipitation occurred until after several minutes an exothermic reaction developed. Such behaviour has not been observed in the corresponding reactions involving titanium, zirconium, niobium, or tantalum chlorides and it appears that the reaction is initiated in the vapour phase. After the ammonium chloride had been filtered off the filtrate was evaporated to dryness and the germanium ester distilled under reduced pressure. In the preparation of the tertiary esters the procedure was modified as follows. The tetrachloride was added with stirring to a solution of the alcohol and pyridine (4 mol./mol. of $GeCl_4$) in benzene (150 c.c.), and reaction was completed by treatment with ammonia. The ester was then isolated as before. The details are given in Table 5 in which all except *n*-alkyl *esters* are new.

(b) *Preparation by alcohol interchange.* The mixture of lower ester, higher alcohol, and benzene (50—100 c.c.) was azeotropically distilled in a column (70 cm.) packed with Fenske glass helices and fitted with a total condensation variable take-off stillhead. A reflux ratio of *ca.* 10 : 1 was used. After removal of solvent, the germanium ester was distilled under reduced pressure. The details are given in Table 5.

TABLE 5.

R in $Ge(OR)_4$	ROH taken (g.)	Starting material: Compd.	Starting material: Taken (g.)	Yield of $Ge(OR)_4$ (g.)	Ge (%): Found	Ge (%): Calc.
Me	15	$GeCl_4$	20	13	37·0	36·9
Et	20	,,	17	16	28·7	28·7
Pr^n	31	,,	15	18	23·5	23·5
Pr^i	20	$Ge(OMe)_4$	12	17	23·2	23·5
Bu^n	40	$GeCl_4$	14	20	19·9	19·9
,, ...	20	$Ge(OEt)_4$	15	20	19·9	,,
Bu^i	50	$GeCl_4$	16	21	19·9	,,
,, ...	20	$Ge(OPr^i)_4$	14	15	19·9	,,
Bu^s	45	$GeCl_4$	12	17	19·9	,,
Bu^t	50	,,	14	19	19·9	19·9
,, ...	30	$Ge(OEt)_4$	10	12	21·4 *	,,
$s\text{-}C_5H_{11}$	40	$GeCl_4$	11	19	17·2	17·2
,, ...	17	$Ge(OPr^n)_4$	11	13	17·3	,,
CMe_2Et	40	$GeCl_4$	15	23	17·2	,,

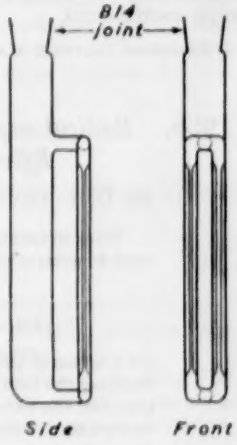
* Calc. for $Ge(OEt)(OBu^t)_3$: Ge, 21·5%.

The yields given in Table 5 are based on the distilled ester.

Density Determinations.—An all-glass dilatometer with two limbs of " Veridia " capillary tubing (bore *ca.* 1 mm.) terminating in standard joints (B 10) was used. Each limb (5 cm.

[13] Holness, *Analyt. Chim. Acta*, 1948, **2**, 254.
[14] Cluley, *Analyst*, 1951, **76**, 523.
[15] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204, 5020.

long) had a fiduciary mark about 1 cm. from the lower end of the capillary, and the dilatometer was calibrated with pure mercury to give the volume v_0 below the fiduciary marks and the average volume per cm. length of capillary (weights were corrected for buoyancy). Before each measurement the dilatometer was cleaned first with nitric–chromic acid, next distilled water, then aqueous sodium hydroxide (10% w/v), and finally it was steamed for $\lt$ 1 hr. It was then dried for 1 hr. at 130° and allowed to cool at 0·05 mm. and dry air was then admitted. After storage in a desiccator (30 min.) it was kept in the balance for 30 min. before being weighed. It was essential to adhere to this rigid procedure to obtain accurately reproducible results. The dilatometer was then connected through a B 10 joint (lubricated with high-vacuum Silicone grease) to an all-glass fractional distillation apparatus and the middle fraction of germanium ester was collected under reduced pressure (0·1 mm.). Enough sample (6·5 c.c.) was collected to bring the level of the meniscus in each capillary just above the fiduciary mark. After admission of dry air the dilatometer was detached, the joints were immediately degreased with trichloroethylene, and the apparatus was reweighed. Experiments on the empty dilatometer showed that the greasing and degreasing procedure did not significantly affect the weight of the dilatometer. The joints were then regreased and the dilatometer was completely immersed in a water-bath thermostatically controlled to $\pm$0·1° for 1 hr. before measurement of the heights of the menisci above the fiduciary marks. Measurements were then made at different temperatures in the following order: 20, 25, 30, 35, 40, 45, 42·5, 37·5, 32·5, 27·5, and 22·5°, 1 hr. being allowed at each temperature for attainment of thermal equilibrium. At least two samples of each compound were used and the reproducibility of the results was about 1 in 10^4. Within this limit of accuracy the densities were exactly linear functions of temperature and the results are presented in Table 6 in the form $d_t = d_0 - \alpha t$ where d_t is the density (g./c.c.) at $t°$ and d_0 and α are constants. Our results are in good agreement with the values at 25° reported by Johnson and Fritz [16] for the *n*-alkyl germanates.



Surface Tensions and Parachors.—The apparatus is shown in the Figure. The "Veridia" capillaries were found by the mercury-thread method to be uniform in bore within 0·01%. The cleaning procedure was similar to that used for the dilatometer except that dry steam was found to be better in the steaming out while in the final drying at 0·05 mm. the apparatus was cautiously "flamed." The sample was collected by distillation at 0·1 mm. and the difference in levels of the menisci was measured at the same temperatures as used for the densities. The apparatus was calibrated with pure benzene. At least two samples of each ester were measured, giving meniscus levels in different regions of the capillaries, and the reproducibility was better than 0·5%. Slight exposure of the sample to the atmosphere gave no visible signs of hydrolysis but the surface tension was markedly affected. Within the experimental error the surface

TABLE 6.

R in $Ge(OR)_4$	d_0	α	R in $Ge(OR)_4$	d_0	α
Me	1·3599	0·00142	Pr^i	1·0515	0·00108
Et	1·1592	0·00122	Bu^i	1·0281	0·00091
Pr^n	1·0820	0·00103	Bu^s	1·0396	0·00093
Bu^n	1·0400	0·00093	Bu^t	1·0844	0·00108
n-C_5H_{11}	1·0156	0·00086	CMe_2Et	1·0662	0·00095

TABLE 7.

R in $Ge(OR)_4$	γ_0	β	R in $Ge(OR)_4$	γ_0	β
Me	24·51	0·0810	Pr^i	22·80	0·0815
Et	25·43	0·0880	Bu^i	25·41	0·0865
Pr^n	25·85	0·0895	Bu^s	25·79	0·0930
Bu^n	26·26	0·0905	Bu^t	24·74	0·0800
n-C_5H_{11}	26·43	0·0890	CMe_2Et	25·76	0·0950

tension of each sample was exactly a linear function of temperature and the results in Table 7 are expressed in the form $\gamma_t = \gamma_0 - \beta t$, where γ_t is the surface tension at $t°$ and γ_0 and β are

[16] Johnson and Fritz, *J. Amer. Chem. Soc.*, 1953, **75**, 718.

constants. The results for the parachor, $[P] = V_m \gamma^{\frac{1}{4}}$, at different temperatures are given in Table 8 together with the root-mean-square percentage deviations (σ) from the mean values given in Table 1.

From the probable error of up to 0·5% in the surface-tension measurements we should expect error in the parachors to be up to 0·1% and it is clear from Table 8 that for each compound the parachor is independent of temperature within the expected error. It is noteworthy that for the *n*-alkyl esters σ decreases with increase in chain length. This trend is not surprising because the ease of hydrolysis appears to decrease with increase in chain length and it is undoubtedly the susceptibility of these compounds to hydrolysis which is the main cause of experimental error.

TABLE 8.

R in $Ge(OR)_4$	[P] 20°	25°	30°	35°	40°	σ	R in $Ge(OR)_4$	[P] 20°	25°	30°	35°	40°	σ
Me	323·2	323·4	323·7	324·0	324·2	±0·11	Pr^i ...	643·6	643·9	644·1	643·6	644·3	0·04
Et	491·2	491·7	492·0	492·3	492·4	0·09	Bu^i ...	797·2	797·2	798·7	797·2	796·6	0·09
Pr^n	644·7	644·9	645·0	644·9	644·0	0·06	Bu^s ...	790·8	790·4	790·0	789·8	789·2	0·07
Bu^n ...	794·8	794·8	794·6	794·4	794·2	0·03	Bu^t ...	—	753·9	754·3	754·0	755·7	0·09
$n\text{-}C_5H_{11}$	939·9	939·7	939·3	939·3	938·7	0·04	CMe_2Et	888·9	888·6	888·0	887·5	886·9	0·08

BIRKBECK COLLEGE, MALET ST., LONDON, W.C.1. [*Received, August 10th*, 1956.]

---

958. *Radical-capture Agents in Tetralin. Measurement of Relative Efficiencies and Correlation with Structure.*

By D. S. DAVIES, H. L. GOLDSMITH, A. K. GUPTA, and G. R. LESTER.

Measurements of the inhibition of the autoxidation of tetralin have been used to determine the relative rates of the radical-capture reaction

$$TO_2\cdot + AH \longrightarrow TO_2H + A\cdot$$

($TO_2\cdot$ = tetralyl peroxide radical : AH = antioxidant)

for a series of simple phenols. Electron-repelling substituents in the phenols increase the rate and electron-attracting ones decrease it. For polyalkylated phenols, the effects of substituents on the logarithm of the rate are additive, except for 2 : 6-substitution. There is a correlation between the energy of the highest occupied molecular orbital in a phenol (as calculated by the non-bonding orbital method) and the rate at which it captures radicals.

SUBSTANCES containing hydrocarbon chains, *e.g.*, petroleum, rubber, edible fats, Polythene, are commonly preserved from oxidative deterioration by addition of antioxidants. It has been established [1-4] that sometimes these oxidations occur by the mechanism

(1) $I \longrightarrow X\cdot$

(2) $X\cdot + RH \longrightarrow R\cdot + XH$

(3) $R\cdot + O_2 \longrightarrow RO_2\cdot$

(4) $RO_2\cdot + RH \longrightarrow RO_2H + R\cdot$ } chain propagation

(5) $RO_2\cdot + RO_2\cdot \longrightarrow$ dead products (termination in absence of antioxidant)

(6) $RO_2\cdot + AH \longrightarrow RO_2H + A\cdot$ (termination in presence of antioxidant)

In this system, I is an initiator (present perhaps by chance) which gives radicals X·; RH is the hydrocarbon suffering oxidation, and AH the antioxidant. For AH to be efficient, reaction (6) must be fast and the derived radical A· must be unable to generate

[1] Bolland and Gee, *Trans. Faraday Soc.*, 1946, **42**, 236.
[2] Bolland and ten Have, *ibid.*, 1947, **43**, 201.
[3] *Idem*, *ibid.*, 1949, **45**, 93.
[4] Bamford and Dewar, *Proc. Roy. Soc.*, 1949, *A*, **198**, 252.

fresh R· radicals from RH. The way in which these properties vary with the structure of AH is therefore of obvious practical as well as theoretical interest. This paper describes the development of an experimental method for measuring radical-capture efficiency in a model oxidation which can be used to investigate as many as possible of the various types of radical-capture agents.

Bolland and ten Have [2] have carried out this type of measurement for a few inhibitors, using the benzoyl peroxide-catalysed autoxidation of ethyl linoleate as their reference system, and Bamford and Dewar [4] used the effects of three inhibitors in elucidating the kinetics of the oxidation of tetralin. Our present method was developed directly from the methods of these authors : tetralin has been the substrate normally used, but measurements have also been carried out with ethyl linoleate.

The main difficulty encountered was the establishment of an initiator system which could be used with the widest possible variety of antioxidants. Photochemical methods were tried, with anthraquinone and its derivatives as photosensitisers, but failed because many inhibitors give coloured products. The photosensitiser solutions also proved inconveniently unstable. In our hands initiation by benzoyl peroxide proved unsatisfactory, partly because this substance can react directly with many of the phenols which were studied (although Bolland and ten Have were able to use it for a limited number of phenols), and partly because the oxidation rates were sensitive to the state of the surface of the reaction vessel. The final choice was azo*iso*butyronitrile (AZDN) which gives radicals by the reaction

$$CN{\cdot}CMe_2{\cdot}N{:}N{\cdot}CMe_2{\cdot}CN \longrightarrow 2CN{\cdot}CMe_2^{\bullet} + N_2$$

at a rate virtually independent of the environment.[5, 6]

Oxidation Kinetics.—Application of the stationary-state method to steps (1)—(4) and (6) of the above reaction scheme leads to the equation

$$-d[O_2]/dt = R_i(1 + k_4[TH]/k_6[AH]) \quad . \quad . \quad . \quad . \quad . \quad (i)$$

so that a plot of $-d[O_2]/dt$ against $1/[AH]$ should give a straight line if R_i, the rate of chain-starting, is constant. Fig. 1 shows two cases in which (i) was tested directly; straight lines were obtained, the intercepts being equal within the experimental error.

The direct testing of (i) is however tedious, and a quicker method of checking the applicability of the reaction scheme is to consider the variation of rate with time during a single experiment. If we assume that the antioxidant is only used in stopping oxidation chains, then under stationary-state conditions

$$[AH] = [AH]_0 - R_i t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

where $[AH]_0$ is the initial concentration. From (i) and (ii)

$$\frac{1}{-d[O_2]/dt - R_i} = \frac{k_6}{k_4[TH]} \cdot \left\{ \frac{[AH]_0}{R_i} - t \right\} \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

If R_i is constant for the period in question, and further if it is negligible compared with $d[O_2]/dt$, then a plot of $1/(-d[O_2]/dt)$ against time should be linear.

As regards the first condition, it is known [5, 6] that approximately 1% of AZDN decomposes in 1 hr. at 50°, so that in these experiments (maximum duration 2 hr.) the amount of initiator could be taken as constant throughout. It is, however, also known [7, 8] that not every radical derived from the decomposition of AZDN starts chains; Bateman and Morris [7] find that the ratio of R_i to the total number of radicals produced in the same time is 0·5 in tetralin at 45°, while in the present work it was found by the same method to be 0·6 at 50°.

[5] Overberger, O'Shaughnessy, and Shalit, *J. Amer. Chem. Soc.*, 1949, **71**, 2661 (cf. Melville and Cooper, *J.*, 1951, 1994).
[6] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1223.
[7] Bateman and Morris, *Trans. Faraday. Soc.*, 1952, **48**, 1149.
[8] Hammond, Sen, and Boozer, *J. Amer. Chem. Soc.*, 1955, **77**, 3244.

For constancy of R_i it is therefore also necessary that this ratio should be constant under the conditions used and unaffected by the presence of an antioxidant. From the results quoted below it seems clear that this condition is, in fact, fulfilled, and Fig. 4 shows that at constant $[AH]_0$ the initial rate of oxidation varies linearly with [AZDN].

The quantity measured in these experiments was the net absorption of gas by the

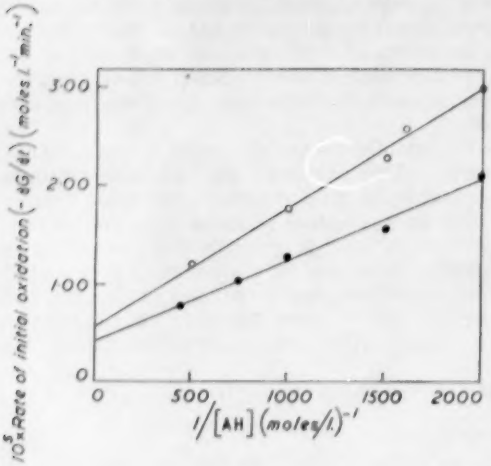


FIG. 1. *[Plot of initial rate of oxidation against* $1/[antioxidant]$.

○ 2-*tert.*-Butyl-4 : 6-dimethylphenol.
● Quinol.

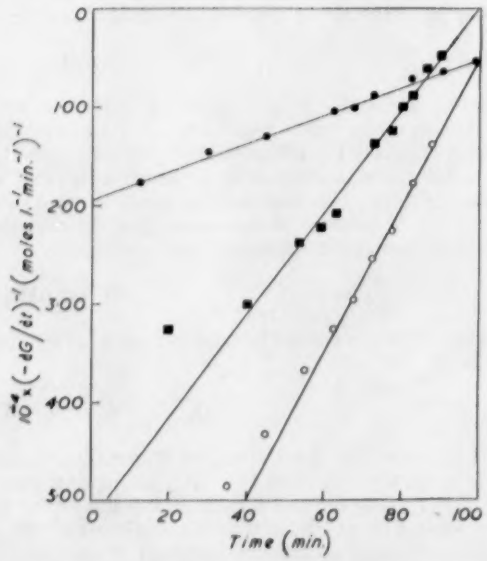


FIG. 2. *Plot of* $(-dG/dt)^{-1}$ *against time* ($[AH]_0$ *constant at* 10^{-2} *mole/l.*).

○ Quinol.
■ 2-*tert.*-Butyl-4 : 6-dimethylphenol.
● 2 : 4-Dimethylphenol.

system, $-dG/dt$, which is of course the resultant of the absorption of oxygen by the tetralin, $-d[O_2]/dt$, the absorption of oxygen by AZDN radicals, and the evolution of nitrogen by decomposing AZDN molecules. If dG'/dt, the sum of the last two terms, and R_i are together negligible compared with the rate of absorption of oxygen by the tetralin, (iii) becomes

$$\frac{1}{-dG/dt} = \frac{k_6}{k_4[TH]}\left\{\frac{[AH]_0}{R_i} - t\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(iv)}$$

This equation held satisfactorily in all cases tested, below a particular antioxidant concentration depending on the activity of the antioxidant, *i.e.*, above a certain rate of oxidation. Fig. 2 illustrates this point; it will be seen that with the two better antioxidants the rates of oxidation are at first too low for (iv) to hold (though the earliest deviations are partly due to initial disturbances of the system), but later, when $(R_i + dG'/dt)$ has become negligible compared with $-d[O_2]/dt$, (iv) is closely followed; (iv) also predicts that the intercept of the $1/(-dG/dt)$ against t line should be $[AH]_0/R_i$ times the slope, and Fig. 3, which gives the results of plotting the slopes against the intercepts measured for a

FIG. 3. *Plot of slopes against intercepts from the* $(-dG/dt)^{-1}$*–time graphs.*

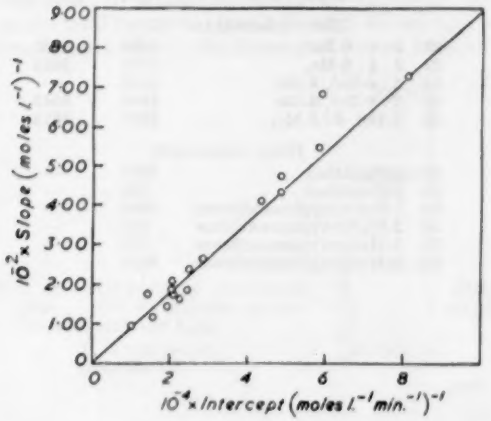
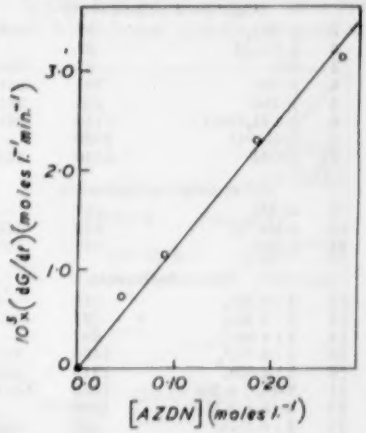


FIG. 4. *Plot of initial rate of oxidation against initiator concentration* ([AH] *constant at* 10^{-3} *mole/l. of* 2-tert.-*butyl*-4 : 6-*dimethylphenol*).



series of antioxidants at constant $[AH]_0$, shows that there is in fact a constant proportionality between the two quantities.

Whilst this work was in progress, Boozer, Hammond, and their co-workers [9] brought evidence to show that with antioxidants of " intermediate activity " the simple hydrogen-abstraction reaction (6) is not the chain-termination step in the inhibited oxidation of tetralin and cumene. This led the authors to postulate a two-stage reaction involving first the reversible formation of a molecular complex between $RO_2^{\bullet}$ and AH, followed by reaction of this complex with another peroxide radical giving inactive products. In the case of phenol and diphenylamine the rate of oxidation was shown to be proportional to $\sqrt{R_i}$ and $1/\sqrt{[AH]}$.

In the present paper phenol and compounds 1 and 2 shown in Table 1 were found to be of such low antioxidant activity that the linear relation between $1/(-dG/dt)$ and time [equation (v)] no longer applies. But for all other compounds listed in the Table there is good evidence that the kinetic scheme and underlying assumptions are sound, and one may therefore consider the antioxidant activities so measured.

Relative Antioxidant Efficiencies.—Table 1 gives the relative values of the rate constant k_6 for capture of tetralyl peroxide radicals, determined in the form of the ratio k_6/k_4 at 50°, for a series of simple phenols.

Effect of varying substituents in the para*-position.* The values for compounds 1—8 show that, in the *para*-position, an electron-releasing substituent (alkoxyl, alkyl groups) generally improves the efficiency and an electron-withdrawing substituent impairs it. The values for the very poor antioxidants phenol, *p*-chlorophenol, and *p*-nitrophenol have

[9] (*a*) Boozer and Hammond, *J. Amer. Chem. Soc.*, 1954, **76**, 3861; (*b*) Boozer, Hammond, *et al.*, *ibid.*, 1955, **77**, 3233; (*c*) *Idem*, *ibid.*, p. 3238.

qualitative rather than quantitative significance, because the rates of oxidation here are becoming close to the " uninhibited " rate, so that termination by reaction (5) cannot be ignored, and because there is some evidence [10] that the phenoxide radicals in these cases may be able to re-start chains.

Effect of polysubstitution by alkyl groups. Polysubstitution by alkyl groups is, as might be expected, more effective than monosubstitution. Moreover, the total effect of the

TABLE 1. *Phenols : Effect of substituents on radical-capture efficiency and hydroxyl band frequency.*

No.	Substituent	k_6/k_4	OH Band frequency ($cm.^{-1}$)	No.	Substituent	k_6/k_4	OH Band frequency ($cm.^{-1}$)
	Single *para*-substituents				Three substituents		
1	*p*-NO_2	52	3597	22	2 : 4 : 6-Bu^t_3	1430	3642
2	*p*-CO_2H	52	—	23	2 : 4 : 6-Me_3	3070	3621
3	(H)	83	3610	24	2 : 4-Bu^t_2, 6-Me	3240	—
4	*p*-Me	291	3610	25	2 : 6-Bu^t_2, 4-Me	1990	3643
5	*p*-Bu^t	464	3614	26	2-Bu^t, 4 : 6-Me_2	3320	3618
6	*p*-$CH_2Ph{\cdot}O$	1710	3616				
7	*p*-$Bu^t{\cdot}O$	2330	—		Other compounds		
8	*p*-OH	5540	3620	27	α-Naphthol	3950	—
				28	β-Naphthol	830	—
	Other single substituents			29	1-Hydroxyphenanthrene	4060	—
9	*m*-Me	193	—	30	2-Hydroxyphenanthrene	437	—
10	*o*-Me	522	3612	31	3-Hydroxyphenanthrene	990	—
11	*o*-Bu^t	787	3609	32	4-Hydroxyphenanthrene	3090	—
	Two substituents						
12	3 : 5-Me_2	545	—				
13	2 : 3-Me_2	591	—				
14	3 : 4-Me_2	697	—				
15	2 : 4-Bu^t_2	1430	3610				
16	2 : 4-Me_2	1310	3616				
17	2-Bu^t, 4-Me	1660	3611				
18	4-Bu^t, 2-Me	1580	—				
19	2 : 6-Bu^t_2	967	3640				
20	2 : 6-Me_2	1110	3621				
21	2-Bu^t, 6-Me	1450	3620				

various groups in a di- or tri-substituted compound on the logarithm of k_6 is usually the sum of the effects of the individual groups in the appropriate monosubstituted phenols. This is shown in Fig. 5. Here, values of $\Delta \log k$ have been set up for the 2-, 3-, and 4-methyl, and 2- and 4-*tert.*-butyl groups, and the rates then calculated for the polysubstituted compounds by simply summing the appropriate logarithm increments. As can be seen, agreement between calculated and observed rates is quite good until substituents are inserted in both the 2- and the 6-position. For all such compounds, the observed rates of chain termination are lower than expected, the discrepancy being especially marked in the case of 2 : 6-di- and 2 : 4 : 6-tri-*tert.*-butylphenols. The interpretation of this seems clear : the alkyl groups influence the ease of fission of the O–H bond by the usual mesomeric effect. This is primarily reflected in the activation energy, E_6, and each group makes its own individual contribution to the lowering of E_6, unperturbed by the presence of other groups.

The mesomeric effect is greatest when the O–H bond lies in the plane of the benzene ring. It is only where two *ortho*-substituents are present that this is unlikely to be the case. When two such groups are present, the conjugation of the *p*-electrons of the oxygen with the π-electrons of the ring will be impaired, and the electronic effects of the substituents will no longer be so simple. Moreover, it is likely that steric factors will become important, and will cause the rate to fall. The chemical properties of the 2 : 6-dialkylated phenols, as is well known, exhibit this " hindrance."

The Infrared Spectra of Phenolic Antioxidants.—In the discussion in the preceding paragraph, it has been tacitly assumed that the hydrogen atom which is concerned in radical

[10] Bolland and ten Have, *Discuss. Faraday Soc.*, 1947, **2**, 252.

capture is that attached to the oxygen atom. If this is true, the properties of the O–H bond must be relevant to antioxidant activity, and the most obvious one to investigate is the force constant for stretching, as revealed by the frequency of the appropriate band in the infrared spectrum. These frequencies have been measured, and are recorded in Table 1.

In the series of *para*-monosubstituted compounds (1—8), there is a progressive increase in the O–H stretching frequency (measured in dilute solution in carbon tetrachloride) with increasingly electron-repelling substituents. Although the effect is not large, it is quite definite: the difference between the extreme cases (*p*-nitrophenol and quinol) is 23 wave-numbers, whilst the limits of resolution are 2—3 wave-numbers. There is, therefore, a correlation between the force-constant for O–H stretching and the radical-capture efficiency. Curiously, the direction of this correlation is the reverse of what might have been expected: [11] active radical-capture agents are presumably those for which the resistance to the total rupture of the O–H bond is *least*, and yet it is now found that in these cases the resistance to small displacements (those brought about by infrared quanta) is *greatest*.

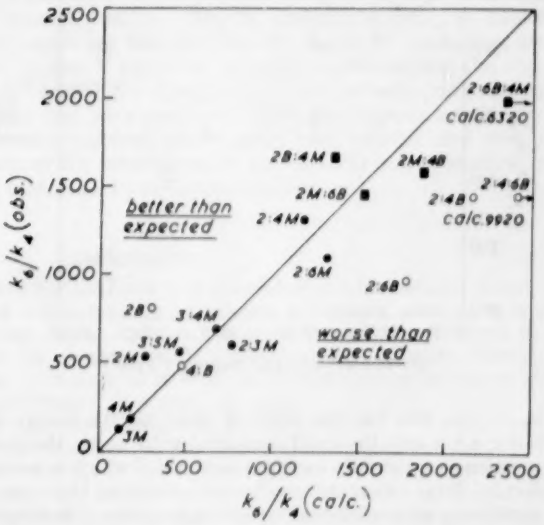


FIG. 5. *Additivity of substituent effects: plot of observed against calculated values of* k_6/k_4.
B = *tert.*-Butyl.
M = Methyl.

Such a state of affairs is of course physically quite possible, but is rather difficult to interpret. For the present, it will not be further discussed.

Correlation of Radical-capture Efficiencies in Different Oxidations.—It is of interest to find out whether variations in the structure of the peroxide radical $RO_2\cdot$ are accompanied by any change in its relative reactivity toward various antioxidants. Table 2 shows a

TABLE 2. *Comparison of radical-capture efficiencies in the autoxidation of tetralin and ethyl linoleate.*

Compound	Relative efficiency in tetralin (50°)	ethyl linoleate (45°)
Quinol	1	1
α-Naphthol	0·75	0·56
β-Naphthol	0·15	0·077

comparison between the present results in tetralin and those of Bolland and ten Have [2] in ethyl linoleate. From this it appears that the efficiencies run parallel and that results are not greatly dependent on the nature of the peroxide radical.

Quantum-mechanical Considerations.—If we accept the view that it is the O–H bond

[11] Cf. Walsh, *Trans. Faraday Soc.*, 1947, **43**, 60.

which participates in the termination reaction, and that variations in antioxidant efficiency are due mainly to changes in the activation energy E_6 of reaction (6), it is possible to consider the effect of structure on antioxidant efficiency, from the quantum-mechanical aspect. If the linear relation between the activation energy and the heat of reaction found in some cases [12] exists here also, then when AH is varied a linear relation may be expected between log k_6 and D_{AH}, the energy of the dissociation of AH into A· and H·, which in turn will depend on the energy U of the most loosely held mobile electron in the compound in question.

The quantity U is very readily evaluated by the non-bonding molecular-orbital method due to Longuet-Higgins [13] and Dewar.[14] If the non-bonding molecular-orbital coefficient = α at that atom in the isoconjugate system which is replaced by oxygen in the hydroxy-compound, the corresponding energy level, in units of β_{cc}, = $\alpha_o^2\delta$ where $\alpha_o = \delta\beta_{co}$ and $\beta_{co} = \beta_{cc}$. If it is desired to distinguish between the magnitudes of β_{co} and β_{cc}, writing

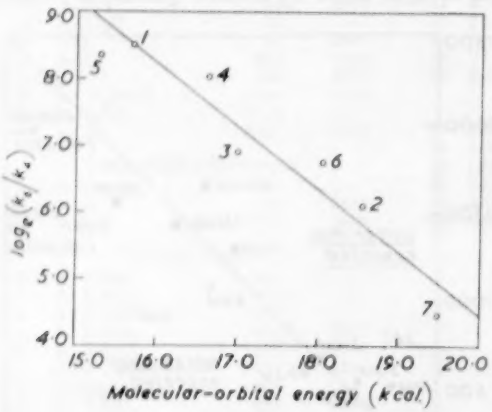


FIG. 6. *Correlation between relative radical capture efficiencies (k_6/k_4) and energies of the highest occupied (non-bonding) molecular orbital.*

(1) 1-Hydroxyphenanthrene.
(2) 2-Hydroxyphenanthrene.
(3) 3-Hydroxyphenanthrene.
(4) 4-Hydroxyphenanthrene.
(5) α-Naphthol.
(6) β-Naphthol.
(7) Phenol.

$\beta_{co} = \gamma\beta_{cc}$, this has the effect of changing the energy level to $\alpha_o^2\delta/\gamma^2[1 - \alpha_o^2(1 - 1/\gamma^2)]$. Since α_o^2 is usually small compared with unity, the parameters enter into the energy expression as a virtually constant factor δ/γ^2 which is irrelevant in a correlation with experimental data. That this method of estimating U is reasonable is demonstrated by carrying out the complete molecular-orbital calculation. Results obtained by Long and Sykes [15] are given in Table 3 and are similar to those of the simplified calculation for the same choice of parameters ($\delta = 2$, $\gamma = 2$).

TABLE 3.

Compound	Energy of highest occupied orbital (units of β) by solution of secular equation	from non-bonding molecular-orbital method
Phenol	0·458	0·500
α-Naphthol	0·307	0·340
β-Naphthol	0·381	0·439

Values of U plotted against log k_6/k_4 in Fig. 6 have been determined by using $\delta/\gamma^2 = 2$. As can be seen, the correlation is good. Again, in a recent paper, Hush [16] found that the changes in unsaturation energy in the formation of phenoxide radicals are related to the standard redox potentials of the phenols as measured by Fieser's "critical potential" method.[17]

[12] Evans and Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.
[13] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 265.
[14] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.
[15] Long and Sykes, *J. Chim. phys.*, 1950, **47**, 361.
[16] Hush, *J.*, 1953, 2375.
[17] Fieser, *J. Amer. Chem. Soc.*, 1930, **52**, 5204.

Further, using the non-bonding molecular-orbital method, he has expressed the change in unsaturation energy in terms of the π-electron densities at the extracyclic oxygen atom and found that these also are related to the redox potentials.

To investigate the effect of substituents from a similar standpoint, we may suppose that they have the effect of changing the electronegativity of the carbon atom to which they are attached. Correspondingly, let the Coulomb integral be changed to $\alpha_0 + \delta\beta$; U may then be calculated in terms of δ, and from the observed relationship between U and $\log k_6/k_4$, and the known values of $\log k_6/k_4$ for the particular compound, δ can be calculated. For the alkyl groups most extensively investigated, methyl and *tert.*-butyl, the δ values are respectively −0·55 and −0·75. Although not much significance can be attached to the precise numerical values, it is reassuring that the sign of the effect is in accordance with the electron-repelling character of these groups.

The effect of *meta*-substituents, *i.e.*, those attached to unstarred atoms, vanishes to a first approximation. But if we include the inductoelectromeric effect [18] with auxiliary inductive parameter [19] = 1/3, then a *meta*-substituent should produce 2/3 of the destabilisation effect of a substituent in an adjacent starred position. This is evident since the two adjacent starred positions have numerically equal coefficients. Finally, it may be shown that when the electronegative effect of the oxygen is explicitly included in determining the charge distribution in the highest occupied orbital, the charge densities at the *meta*-positions are of the order of 1/5 of those for *ortho*- and *para*-positions. Now this appears insufficient to explain an appreciable direct *meta*-substituent effect on its own account and we must conclude that the inductive effect of the substituent at the adjacent active atoms is the main reason for the existence of activation by *meta*-substitution.

Experimental

Materials.—Tetralin was purified by shaking it with concentrated sulphuric acid to remove hydroperoxide, dried, and refluxed over sodium for a few hours in nitrogen, after which it was distilled through a 35-plate Vigreux column. Before use residual impurities (believed to be traces of metals) were removed by passing small amounts of the distillate through a 2 cm. × 3 cm. column of alumina. The material so obtained showed a negligible rate of oxidation at 50° in the absence of added initiator; b. p. 205°, n_D^{20} 1·5411.

Azo*iso*butyronitrile (AZDN), recrystallised from ether, had m. p. 103°.

Antioxidants were purified by distillation or recrystallisation from suitable solvents.

Method.—The oxidation was carried out in small Warburg-type manometers with dibutyl phthalate as the manometric liquid. The tetralin solutions were contained in 10 c.c. glass cells which were connected to the manometer *via* a standard glass joint and a glass spiral (flexible enough to allow the cell to be efficiently shaken on an eccentric), the whole assembly being immersed in a thermostat normally at 50°. Shaking was always rapid enough to ensure that transfer of oxygen was not rate-controlling. In making up the solutions, initiator was first weighed into the cell, followed by tetralin from a microburette, and a solution of antioxidant in tetralin from a microsyringe to make up the volume to 2·00 ml. This enabled very small quantities of antioxidant (10^{-3}—10^{-4} mole/l.) to be accurately introduced. The movement of the manometer liquid was observed with a cathetometer, and from time to time the level was readjusted by admitting more air or oxygen into the bulb.

The authors thank Mr. M. N. Berger for work done in the early stages of this research, and express their appreciation of helpful discussions with the late Professor M. G. Evans, Sir Cyril Hinshelwood, and Professor H. W. Melville. They are indebted to Mr. M. St. C. Flett for the infrared absorption measurements.

Imperial Chemical Industries Ltd., Dyestuffs Division,
Hexagon House, Blackley, Manchester 9. [*Received, February 27th*, 1956.]

[18] Brown and Dewar, *J.*, 1953, 2406.
[19] Brown, *Quart. Reviews*, 1952, **6**, 63.

959. *Kinetics and Mechanism of Bromination of Phenol with Bromine and Iodine Bromide in Glacial Acetic Acid and Carbon Tetrachloride.*

By Lourdu M. Yeddanapalli and N. S. Gnanapragasam.

The kinetics of reaction of phenol with (*a*) bromine and (*b*) iodine monobromide in acetic acid and carbon tetrachloride has been studied by a method applicable to short reaction times. Reaction (*a*) in acetic acid is of first order with respect to phenol and bromine severally. The other brominations are of first order with respect to phenol and of second order with respect to reagent. Activation energies are calculated. Reaction (*b*) in both solvents is catalysed by iodine monobromide (not by iodine). Reaction mechanisms are discussed.

The main difficulty in the kinetic investigation of the bromination of phenol by bromine appears to be the extreme rapidity of the reaction even at low concentrations. Robertson *et al.*[1] reported that reaction of 0·001M-phenol and bromine in anhydrous acetic acid is 20% complete in 0·82 min. Two possible ways of rendering the reaction tractable seemed to be the use of a milder brominating agent, and the modification of the experimental procedure to permit of rate-measurements within intervals of seconds. Iodine monobromide was found, in our investigations of cashew phenols,[2] to be a mild brominating agent for the phenolic nucleus: it is known to react with phenol in non-aqueous solvents, such as glacial acetic acid and carbon tetrachloride, to give only *p*-bromophenol.[3,4] Its use and a modified experimental procedure are now reported, reaction being carried out in acetic acid and in carbon tetrachloride. For additional information, bromination of anisole in the latter solvent was included. Fresh experimental data have also been obtained regarding the disputed rôle of iodine as catalyst in bromination of phenol.[4,5]

Experimental

Procedure.—The halogen and phenol solutions (5 c.c. each), in several glass-stoppered bottles and corked test-tubes respectively, were placed in a thermostat maintained within ±0·05°. After the solutions reached the bath-temperature, the phenol solution was quickly emptied into the halogen solution, and the mixture was allowed to react for a definite time, even as short as 5 sec., after which the reaction was arrested by quick addition of potassium iodide solution, the liberated iodine being titrated against standard sodium thiosulphate.

Glacial acetic acid (*f.* p. 15·8°) was used without treatment. Anhydrous carbon tetrachloride was prepared by fractionation of a sulphur-free B.P. quality sample (*b.* p. 76·5—76·7°/760 mm.).

Reproducibility is illustrated by the duplicate results 50·4 and 49·9 for the first entry in the second column of Table 3, and 55·8 (twice) for the second entry there.

Results in Acetic Acid.

Phenol–Bromine Reaction.—(a) *Over-all order.* Rate-measurements were made with phenol and bromine in acetic acid over the concentration range 0·001—0·02M. Fig. 1 and Table 1 show the results. The total order of the reaction (see Table 1) is evidently two.

(b) *Individual orders.* Ostwald's isolation method was employed for evaluating the kinetic order with respect to bromine. The concentration of phenol was kept at a constant large excess, 0·02M, and that of bromine varied from 0·002 in the first to 0·001M in a second experiment. The time required for a definite fraction of the reaction was found to be independent of the initial concentration of bromine, so that the order with respect to bromine is one.

[1] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.
[2] Paul, M.Sc. Thesis, Madras, 1951; Yeddanapalli and Paul, *J. Sci. Ind. Res.* (*India*), 1953, **12**, *B*, 524.
[3] Militzer, *J. Amer. Chem. Soc.*, 1938, **60**, 256.
[4] Bennett and Sharpe, *J.*, 1950, 1383.
[5] Lambourne and Robertson, *J.*, 1947, 1167.

TABLE 1. *Total order of the reaction between phenol and bromine.*

Solvent : acetic acid. Temp. : 30°.

Br reacted (%)	a (mole/l.)	b (mole/l.)	t_1 (sec.)	t_2 (sec.)	n (total order)	Br reacted (%)	a (mole/l.)	b (mole/l.)	t_1 (sec.)	t_2 (sec.)	n (total order)
40	0·020	0·010	4	9	2·17	40	0·004	0·002	26	50	1·94
60	0·020	0·010	10	23	2·20	50	0·004	0·002	40	75	1·91
40	0·010	0·005	9	20	2·15	20	0·002	0·001	19	42	2·14
60	0·010	0·005	23	53	2·20	40	0·002	0·001	50	99	1·99

Rate-measurements were also made with phenol concentrations of 0·02—0·01M, that of bromine being constant at 0·001M. The rate of the reaction can be represented by

$$d[C_6H_4Br{\cdot}OH]/dt = k(a - x)^n(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a and b are the initial concentrations of phenol and bromine respectively, x the amount of each reacted in time t, and n the order with respect to phenol. When 40% of the bromine

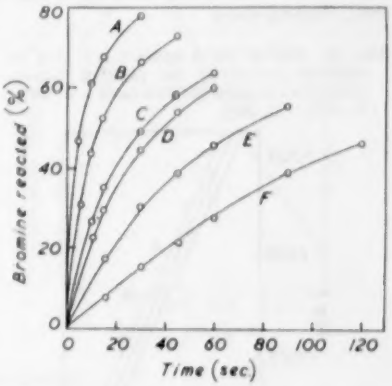


FIG. 1. *Rate of bromination of phenol at various initial equimolar concentrations. A*, 0·02M; *B*, 0·01M; *C*, 0·005M; *D*, 0·004M; *E*, 0·002M; *F*, 0·001M.

has reacted, x is only 0·0004M and therefore negligible when compared to a, 0·02 and 0·01M. Eqn. (1) then reduces to :

$$d[C_6H_4Br{\cdot}OH]/dt = k'(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k' is a first-order rate constant and is equal to ka^n. The values of k' are $8{\cdot}8 \times 10^{-3}$ and $4{\cdot}7 \times 10^{-3}$ at $a = 0{\cdot}02$ and 0·01M respectively. From this n is found to be 0·91, so that the order with respect to phenol is one.

(c) *Activation energy.* Rate constants corresponding to 20%, 25%, and 30% reaction were calculated for phenol and bromine (0·001M each) over the temperature range 20—40°. Fig. 2 shows plots of log k against $1/T°(K)$. From the slopes the calculated activation energies are 4·81, 4·81, and 4·88 kcal. mole^{-1} for 20, 25, and 30% reaction respectively, the average being $4{\cdot}83 \pm 0{\cdot}05$ kcal. mole^{-1}.

It may be noted that the time required for 20% bromine consumption at 0·001M at 25° in glacial acetic acid in our case, *viz.*, 0·80 min., agrees with the value 0·82 min. in anhydrous acetic acid reported by Robertson *et al.*[1]

Phenol–Iodine Bromide Reaction.—(a) *Over-all kinetic order.* Iodine bromide of the required concentration was prepared by mixing equal volumes of equimolar solutions of iodine and bromine in glacial acetic acid. The reaction between phenol and iodine bromide was found to be homogeneous (as tested by a four-fold increase of surface : volume ratio by addition of small pieces of glass tubing), and not light-sensitive. In order to evaluate the over-all kinetic order, rate-measurements were made with equimolar 0·001—0·1M-solutions of phenol and reagent. The percentage of halogen reacted at each concentration was plotted against time and from the curves the times required for definite fractions of the reaction at different initial concentrations were read off. These together with the calculated kinetic orders are represented in Table 2, from which it is seen that the over-all order is three.

(b) *Individual orders.* The order with respect to iodine monobromide was determined by keeping the phenol concentration at 0·1M and changing that of the reagent from 0·01 to 0·005M. The times required for 20% of the halogen to react in the two cases were 70 and 139 sec. respectively, from which the calculated kinetic order is 1·99. The kinetic order for phenol was determined by the same procedure as with bromine, the iodine bromide being 0·005M and

TABLE 2. *Total order of reaction between phenol and iodine bromide.*

Solvent: acetic acid. Temp.: 30°.

Halogen reacted (%)	*a* (mole/l.)	*b* (mole/l.)	t_1 (sec.)	t_2 (sec.)	*n* (total order)	Halogen reacted (%)	*a* (mole/l.)	*b* (mole/l.)	t_1 (sec.)	t_2 (sec.)	*n* (total order)
16	0·100	0·050	7	26	2·89	12	0·020	0·010	51	216	3·08
20	0·100	0·050	21	91	3·12	16	0·020	0·010	156	645	3·05
12	0·050	0·025	8	29	2·86	8	0·010	0·005	69	276	3·00
16	0·050	0·025	26	100	2·94	4	0·002	0·001	810	3450	3·09

phenol 0·1—0·05M. The values of the second-order rate constants *k'* are 1·02 and 1·05 l. mole^{-1} sec.$^{-1}$ at $a = 0·1$ and 0·05M respectively, so that the order with respect to phenol is 0·87, close to unity.

FIG. 2. *Plot of* log *k against* $1/T$ (°K) *for different extents of the reaction between phenol and bromine* (0·001M *each*): *A*, 30%; *B*, 25%; *C*, 20%.

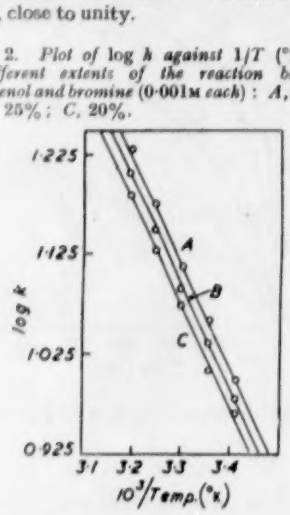
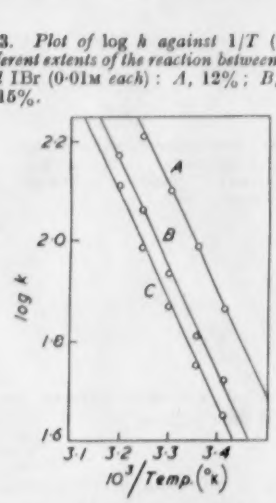


FIG. 3. *Plot of* log *k against* $1/T$ (°K) *for different extents of the reaction between phenol and* IBr (0·01M *each*): *A*, 12%; *B*, 14%; *C*, 15%.



(c) *Activation energy.* Rate constants for the reaction at 0·01M-concentrations at 20—40° were calculated from experimental data for different extents of the reaction. The activation energies calculated from the slopes for 12, 14, and 15% reaction (Fig. 3) are 9·76, 9·71, and 9·69 kcal. mole^{-1} respectively, average 9·72 ± 0·04 kcal. mole^{-1}.

(d) *Iodine bromide catalysis.* In order to examine the effect of iodine on the rate of bromination experiments were made in which the concentration of iodine was progressively increased

TABLE 3. *Effect of iodine on rate of bromination of phenol.*

Solvent: acetic acid. Temp.: 30°. Initial concns.: phenol, 0·01M; bromine, 0·005M.

Concn. of added iodine (M)	Br reacted (%) in first 15 sec.	Total I / Total Br	Concn. of added iodine (M)	Br reacted (%) in first 15 sec.	Total I / Total Br
0·0000	50·4	0·0	0·0040	21·2	0·8
0·0005	55·8	0·1	0·0050	7·5	1·0
0·0010	59·9	0·2	0·0075	2·0	1·5
0·0020	55·5	0·4	0·0100	0·5	2·0
0·0030	37·0	0·6			

from 0 to 0·01M, the phenol and bromine solutions being constantly 0·01M and 0·005M respectively. The results are summarised in Table 3. Column 2 gives the percentage of bromine reacted within the first 15 sec. for varying amounts of added iodine, and column 3 the

ratio of total iodine to bromine. From Fig. 4, which represents the plot of the percentage of bromine reacted against the iodine : bromine ratio, it is seen that the rate of bromination is a maximum when this ratio is 0·31. The significance of this maximum rate may be brought out by the following considerations. It is known that the equilibrium constant for the reaction $I_2 + Br_2 \rightleftharpoons 2IBr$ in an acid medium is quite large, *e.g.*, $5{\cdot}26 \times 10^4$ at 25° in 4N-hydrobromic acid.[6] It may therefore be assumed that in acetic acid the iodine added to bromine will be present almost wholly as IBr. Since the concentration of total bromine is 0·005M and the ratio of total iodine to bromine at the catalytic maximum is 0·31, the iodine concentration corresponding to this maximum will be 0·31 × 0·005, *i.e.*, 0·00155M. Given that each iodine molecule I_2 gives two IBr, the concentration of the latter is 0·0031, so that free bromine is equal to total bromine 0·005 minus the bound bromine 0·00155, *i.e.*, 0·00345M. The ratio, then, of IBr to free bromine becomes 0·0031/0·00345, equal to 0·9, approximately one. It may therefore be concluded that the maximum rate corresponds to the presence of equimolar amounts of IBr and free bromine. In other words, IBr appears to be the catalyst in this bromination.

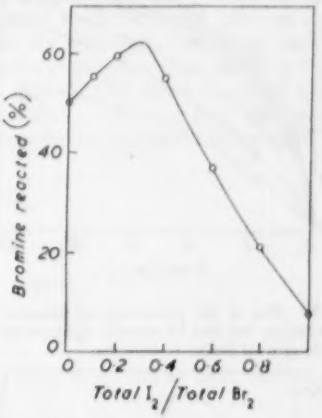


FIG. 4. *Plot of the percentage of bromine reacted in the first 15 seconds against the ratio of total iodine to bromine.*

Results in Carbon Tetrachloride.

Phenol–Iodine Bromide Reaction.—(a) *Kinetic order.* The reaction is not light-sensitive and not sensibly affected by a four-fold increase in surface : volume ratio and so essentially homogeneous. The kinetic order of the reaction is three in the concentration range 0·02—0·002M (see Table 4). Experiments with 0·05M-, 0·05M-, and 0·025M-phenol and 0·005M-, 0·0025M-, and 0·0025M-iodine bromide respectively showed that the time required for 6% halogen consumption in the three cases was 30, 60, and 123 sec. respectively, from which the kinetic order was found to be two with respect to iodine bromide and 1·04 with respect to phenol.

TABLE 4. *Total order of the reaction between phenol and iodine bromide.*

Solvent : carbon tetrachloride. Temp. : 30°.

Halogen reacted (%)	*a* (mole/l.)	*b* (mole/l.)	t_1 (sec.)	t_2 (sec.)	*n* (total order)	Halogen reacted (%)	*a* (mole/l.)	*b* (mole/l.)	t_1 (sec.)	t_2 (sec.)	*n* (total order)
9	0·020	0·010	39	170	3·12	6	0·010	0·004	76	458	2·96
12	0·020	0·010	90	360	3·00	2	0·004	0·002	60	245	3·03
3	0·010	0·004	22	140	3·02	4	0·004	0·002	205	720	2·81

(b) *Activation energy.* The halogen consumption on reaction of phenol and iodine bromide (0·01M each) in the temperature range 0—40° is represented in Fig. 5, which shows a slight increase in rate from 0° to 20°, but a marked decrease between 20° and 40°. To determine the exact temperature of this rate inversion, third-order rate constants for 10% of the reaction at different temperatures (Table 5) are plotted against temperature in Fig. 6 which shows the inversion to occur at 19°. The apparent activation energy calculated from the rate constants at 0—10° for 10, 14, and 18% reaction is 3·38, 3·46, and 3·49 respectively, the average being

[6] Faull, *J. Amer. Chem. Soc.*, 1934, **56**, 522.

TABLE 5. *Rate constants at various temperatures for phenol–iodine bromide reaction.*

Solvent: carbon tetrachloride. Phenol and IBr, 0·01M each. Extent of reaction: 10%.

Temp.	0°	5°	10°	20°	30°	35°	40°
k_2 (l.² mole⁻² sec.⁻¹)	79·8	88·6	99·6	112·6	48·5	30·7	18·3

3·44 ± 0·06 kcal. mole⁻¹. Similarly at 30—40° E for 6, 8, and 10% reaction is −18·55, −18·42, and −18·42 respectively (average −18·46 ± 0·10 kcal. mole⁻¹).

FIG. 5. *Rate of halogen consumption at various temperatures for phenol–IBr reaction at 0·01M-concentration.*

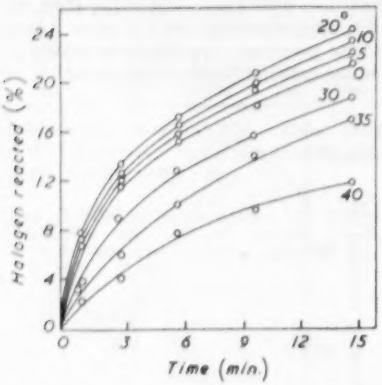


FIG. 6. *Plot of third-order rate-constants for phenol–IBr reaction against temperature.*

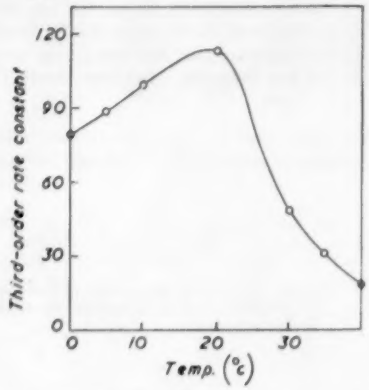


FIG. 7. *Plot of the percentage of bromine reacted in the first 15 seconds against the ratio of total iodine to bromine.*

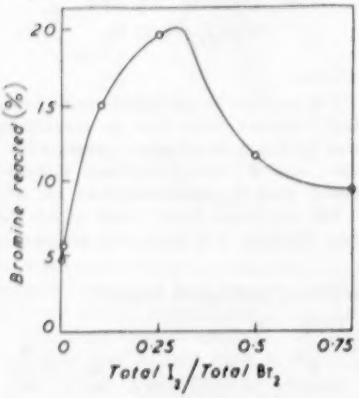
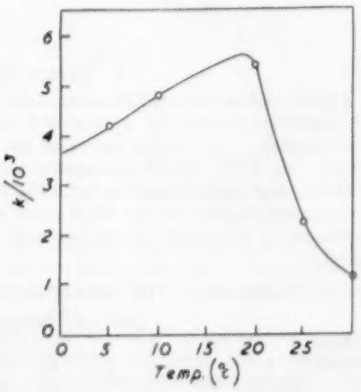


FIG. 8. *Plot of third-order rate-constants for phenol–bromine reaction against temperature* (k at 0° c = 3·7 × 10⁻³).



(c) *Iodine bromide catalysis.* The rate of bromination of phenol in presence of 0—0·01M-iodine, phenol and bromine being constant at 0·01M and 0·005M respectively, was determined in the same manner as in the case of acetic acid. The percentage of bromine which reacted in the first 15 sec. for various amounts of added iodine is represented in Fig. 7 from which the maximum rate is seen to correspond to an iodine : bromine ratio of 0·30. The equilibrium constant at 25° for the reaction $I_2 + Br_2 \rightleftharpoons 2IBr$ in carbon tetrachloride is reported by Yost *et al.*[7] as 363·1, and its heat of reaction[8] as −3260 cal. mole⁻¹. The value of K at 30° calculated from these data is 331·6, so that the concentrations of iodine bromide and free bromine at the catalytic maximum are, respectively, 0·0030M and 0·0035M, from which the ratio of iodine bromide to free

[7] Yost, Anderson, and Skoog, *J. Amer. Chem. Soc.*, 1933, **55**, 552.
[8] Blair and Yost, *ibid.*, p. 4489.

bromine is 0·85, approximately unity. Hence, it may be concluded that the rate of bromination of phenol in carbon tetrachloride is a maximum when iodine bromide and free bromine are in equimolar concentrations, as in the case of acetic acid.

Phenol–Bromine Reaction.—The over-all kinetic order of this reaction between 0·002M and 0·001M is three. It shows the same peculiar temperature effect as the phenol–iodine bromide reaction, with an inversion point at 19° (Fig. 8). The value of E at 0—10° is 3·24 and at 25—30° −24·37 kcal. mole^{-1}.

Anisole–Iodine Bromide Reaction.—This reaction, which is also kinetically of the third order, has a negative temperature coefficient at 20—40°. The third-order rate constants for 2% reaction at 0·01M-anisole and -iodine bromide are 0·90, 0·70, and 0·56 l.^{2} mole^{-2} sec.$^{-1}$ at 30°, 35°, and 40° respectively, from which E is found to be −8·89 kcal. mole^{-1}.

Discussion

Mechanism in Glacial Acetic Acid.—Phenol–bromine reaction. The general mechanism of aromatic bromination in acetic acid solution proposed by Robertson [9] involves a direct electrophilic attack by a neutral bromine molecule on the aromatic compound, forming an intermediate of the type $ArH{\cdot}Br_2$, in which the bromine molecule is polarised into Br^+Br^-. This is followed by the slow rate-determining step, namely, the removal of the bromide ion Br^- from the intermediate complex, leading to $ArHBr^+$. The final step, elimination of a proton from $ArHBr^+$, is a fast reaction, as was demonstrated earlier by Melander.[10] The following is the sequence of reactions :

$$ArH + Br_2 \rightleftharpoons ArH,Br_2 \quad . . . . . (3)$$

$$ArH{\cdot}Br_2 \xrightarrow{Slow} ArHBr^+ + Br^- \quad . . . . . (4)$$

$$ArHBr^+ \xrightarrow{Fast} ArBr + H^+ \quad . . . . . (5)$$

$$H^+ + Br^- \xrightarrow{Fast} HBr \quad . . . . . (6)$$

The intermediate molecular complex shown in eqn. (3) is supposed to have the following resonance structures :

(I) (II) (III)

It is rather difficult to see how (I)—(III) can be called resonance structures at all. Structure (I) represents a polarised benzene molecule and a neutral bromine molecule, there being no chemical bond between them. Structure (III) again represents two separate entities, namely, the positively charged ion $C_6H_5X^+Br$ and a bromide ion Br^-. Structures (I) and (III) therefore correspond to the configuration of the molecular species on the left-hand side of eq. (3) and the right hand side of eqn. (4) respectively. Hence we have to conclude that the intermediate proposed by Robertson must have structure (II).

Now, 1 : 1 molecular complexes between aromatic compounds and halogens, similar to structure (II), have been shown to exist in an inert solvent such as carbon tetrachloride by Keefer and his co-workers [11] by spectrophotometric studies. But there is no experimental evidence for such complexes in a polar solvent such as acetic acid : in fact, experimental evidence shows that in acetic acid the halogens are polarised into X^+X^- by solvation.[12] Nevertheless, one may consider structure (II) to represent the configuration of the activated complex in the reaction.

[9] Robertson, *J.*, 1954, 1267.
[10] Melander, *Arkiv Kemi*, 1950, **2**, 213.
[11] (*a*) Keefer and Andrews, *J. Amer. Chem. Soc.*, 1950, **72**, 4677, 5170; Andrews and Keefer, *ibid.*, 1951, **73**, 462; (*b*) Keefer, Blake, and Andrews, *ibid.*, 1954, **76**, 3062; (*c*) Keefer and Andrews, *ibid.*, 1955, **77**, 2164; (*d*) Ogimaschi, Andrews, and Keefer, *ibid.*, p. 4202.
[12] Fairbrother, *J.*, 1948, 1051; Bayliss, *Nature*, 1949, **163**, 764; Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

In view of these considerations, the following scheme is proposed for the mechanism of bromination of phenol in glacial acetic acid:

$$C_6H_5{\cdot}OH + Br_2 \xrightarrow[\text{Slow}]{k} \underset{\text{Activated complex}}{[C_6H_5{\cdot}OH^+Br^-Br]} \longrightarrow C_6H_5{\cdot}OH^+Br + Br^- \quad . \quad (7)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + Br^- \xrightarrow[\text{Fast}]{} HBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

The rate of production of monobromophenol is given by:

$$d[C_6H_4Br{\cdot}OH]/dt = k[C_6H_5{\cdot}OH][Br_2] \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in agreement with the observed second-order kinetics for the reaction and the orders with respect to phenol and bromine, namely, one each. The experimental value of 4·83 kcal. mole^{-1} for the activation energy evidently refers to the rate-determining step, eqn. (7). The small value of the energy of activation is in keeping with the extremely fast rate of bromination of phenol by bromine (cf. Fig. 1).

Phenol–iodine bromide reaction. As pointed out above, iodine bromide is a brominating agent for phenol in glacial acetic acid and in carbon tetrachloride; it is so even in nitrobenzene, so that the reacting halogen seems to be bromine. The mechanism proposed by Militzer [3] for this reaction in carbon tetrachloride, as represented by:

$$C_6H_5{\cdot}OH + IBr \longrightarrow p\text{-}C_6H_4Br{\cdot}OH + HI \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$HI + IBr \longrightarrow I_2 + HBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

has been criticised by Bennett and Sharpe [4,13] on the ground that it involves polarisation into I^-Br^+, contrary to the greater electropositive character of iodine than of bromine. They suggested therefore that bromine arising by thermal dissociation of iodine bromide is the actual brominating agent, iodine probably acting as catalyst.

Iodine bromide is known to dissociate to about 9·5% at 25° in carbon tetrachloride,[7] but to a much smaller extent in an acid medium such as hydrobromic acid.[6] In acetic acid also, dissociation will be small, as shown by the fact that bromination by bromine is much faster than that by iodine monobromide (the times required for 16% reaction at 0·01M-concentration in acetic acid are about 2 sec. for bromine, cf. curve *B*, Fig. 1, and 645 sec. for iodine bromide, cf. Table 2). But Bennett and Sharpe's suggestion that iodine may be a catalyst in this reaction is against our experimental results (cf. above) that the addition of iodine beyond a critical amount retards the reaction and that in fact iodine bromide is the effective catalyst, as also suggested earlier by Robertson [5] in connection with his criticism of Militzer's mechanism.

In keeping with the above considerations and our experimental results, the following mechanism is suggested:

$$2IBr \rightleftharpoons I_2 + Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$Br_2 + C_6H_5{\cdot}OH \xrightarrow[\text{Slow}]{k} [C_6H_5{\cdot}OH^+Br^-Br] \xrightarrow{IBr} C_6H_5{\cdot}OH^+Br + IBr_2^- \quad . \quad (13)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + IBr_2^- \xrightarrow[\text{Fast}]{} HBr + IBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Taking into account eqns. (13), (8), and (14) the rate of bromination is given by:

$$d[C_6H_4Br{\cdot}OH]/dt = k[C_6H_5{\cdot}OH][Br_2][IBr] \quad . \quad . \quad . \quad . \quad (15)$$

This rate equation, including equimolar concentrations of iodine monobromide and free bromine, accounts for the catalytic maximum observed when the ratio of iodine bromide to free bromine is unity. With iodine bromide as the brominating agent, as in the present

[13] Sharpe, *J.*, 1953, 3713.

case, eqn. (12) must also be taken into account, so that the concentration of bromine is evidently given by the expression $[IBr]\sqrt{K}$, and eqn. (15) then becomes

$$d[C_6H_4Br{\cdot}OH]/dt = [C_6H_5{\cdot}OH][IBr]^2k\sqrt{K} \quad . \quad . \quad . \quad . \quad (16)$$

in agreement with the experimental finding that the total kinetic order is three, two with respect to iodine monobromide and one with respect to phenol.

As seen from the above reaction scheme, the observed activation energy is made up of the heat of dissociation of two moles of iodine bromide [eqn. (12)] and the true activation energy of the rate-determining step [eqn. (13)]. The latter value may be assumed to be the same as for the phenol–bromine reaction, namely, 4·83 kcal. mole^{-1}, since the rate-determining step is essentially the same in both cases. The heat of dissociation of 2 moles of iodine bromide is then equal to the observed activation energy minus the true activation energy, *i.e.*, 9·72—4·83 = 4·89, *i.e.*, 2·45 kcal. per mole. This is of the same order of magnitude as found from vapour-pressure determinations [8] in carbon tetrachloride, *viz.*, 1·63 kcal. mole^{-1}.

Mechanism in Carbon Tetrachloride.—The bromination of benzene and toluene in carbon tetrachloride has been explained by Tsurata *et al.*[14,15] by a mechanism in which the rate-determining step involves the removal of hydrogen bromide from a 1 : 1 bromine–hydrocarbon complex under the catalytic influence of iodine bromide :

$$C_6H_6 + Br_2 \rightleftharpoons C_6H_6{,}Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

$$C_6H_6{,}Br_2 + m\text{IBr} \xrightarrow[\text{Slow}]{} C_6H_5Br + HBr + m\text{IBr} \quad . \quad . \quad . \quad (18)$$

Experimentally m is found to be 3 for benzene [14] and toluene,[15] and 2 for mesitylene.[16] In the case of phenol, we find that the rate is a maximum when iodine bromide and free bromine are present in equimolar concentrations, so that for IBr-catalysed bromination of phenol in carbon tetrachloride m is unity, and the rate-determining step may be represented by :

$$C_6H_5{\cdot}OH{,}Br_2 + IBr \xrightarrow[\text{Slow}]{} C_6H_5{\cdot}OH^+Br + IBr_2^- \quad . \quad . \quad . \quad (19)$$

The observed decrease in the over-all rate of the reaction between 20° and 40° must be attributed to the decrease, with temperature, of the concentration of one of the two reactants in the above rate-determining step. This cannot be iodine bromide, since the same effect is observed for bromination by bromine. Hence the other reactant, namely, the phenol–bromine complex, must be responsible for the negative temperature coefficient. Experimental evidence for the thermal decomposition of hydrocarbon–halogen complexes has recently been provided by spectrophotometric studies,[11b,c] *e.g.*, the value of equilibrium constant for mesitylene–bromine complex at 20° and 25° is 0·398 and 0·381 respectively. It is reasonable to conclude that the phenol–bromine complex begins to dissociate sensibly above 19°, in order to account for the observed negative temperature coefficient. It may be recalled that the negative temperature coefficient in the well-known third-order gas-phase reaction between nitric oxide and oxygen is also attributed [17] to the thermal decomposition of the intermediate $(NO)_2$.

Phenol–bromine reaction. In the light of the above discussion, the following mechanism is proposed for the phenol–bromine reaction in carbon tetrachloride :

$$C_6H_5{\cdot}OH + Br_2 \overset{K'}{\rightleftharpoons} C_6H_5{\cdot}OH{,}Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$C_6H_5{\cdot}OH{,}Br_2 + Br_2 \xrightarrow[\text{Slow}]{k} C_6H_5{\cdot}OH^+Br + Br_3^- \quad . \quad . \quad . \quad . \quad (21)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + Br_3^- \xrightarrow[\text{Fast}]{} HBr + Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

[14] Tsuruta, Sasaki, and Furukawa, *J. Amer. Chem. Soc.*, 1952, **74**, 5995.
[15] *Idem*, *ibid.*, 1954, **76**, 994.
[16] Blake and Keefer, *ibid.*, 1955, **77**, 3707.
[17] Bodenstein, *Helv. Chim. Acta*, 1935, **18**, 743; Rice, *J. Chem. Phys.*, 1936, **4**, 53.

The rate of formation of monobromophenol is given by :

$$d[C_6H_4Br{\cdot}OH]/dt = kK'[C_6H_5{\cdot}OH][Br_2]^2 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

which agrees with the observed third-order kinetics of the reaction.

The molecular complex, $C_6H_5{\cdot}OH,Br_2$, may be assumed to suffer little dissociation between 0° and 10°. It is reasonable therefore to regard the observed activation energy of 3·24 kcal. mole^{-1} in this temperature range as the real activation energy of the rate-determining step [eqn. (21)]; but beyond the inversion point (19°) the complex undergoes thermal dissociation with a consequent decrease of the reaction rate; hence the observed negative activation energy of −24·37 kcal. mole^{-1} between 25° and 30°. This value, as seen from the above reaction scheme, represents the sum of the activation energy of the rate-determining step [eqn. (21)] and the heat of formation of the complex [eqn. (20)], so that we have

$$-24{\cdot}37 \text{ (obs. } E) = 3{\cdot}24 \text{ (true } E) + \Delta H\text{(heat of formation of the complex)} \quad (24)$$

from which ΔH is −27·61 kcal. mole^{-1}. This seemingly high value is not unreasonable in view of the extreme reactivity of phenol in bromination, and the known direct relation between the rate of halogenation of aromatic compounds and the negative heats of formation of their halogen complexes.[11c]

Phenol–iodine bromide reaction. The mechanism of this reaction must include the thermal dissociation of iodine bromide and also its participation, as catalyst, in the rate-determining step. The following scheme seems to satisfy these requirements :

$$2IBr \overset{K}{\rightleftharpoons} I_2 + Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$C_6H_5{\cdot}OH + Br_2 \overset{K'}{\rightleftharpoons} C_6H_5{\cdot}OH,Br_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$C_6H_5{\cdot}OH,Br_2 + IBr \xrightarrow[\text{Slow}]{k} C_6H_5{\cdot}OH^+Br + IBr_2^- \quad . \quad . \quad . \quad (19)$$

$$C_6H_5{\cdot}OH^+Br \xrightarrow[\text{Fast}]{} C_6H_4Br{\cdot}OH + H^+ \quad . \quad . \quad . \quad . \quad (8)$$

$$H^+ + IBr_2^- \xrightarrow[\text{Fast}]{} HBr + IBr \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The rate of the reaction as given by eqns. (20), (19), (8), and (14) is

$$d[C_6H_4Br{\cdot}OH]/dt = kK'\,[C_6H_5{\cdot}OH][Br_2][IBr] \quad . \quad . \quad . \quad . \quad (25)$$

which agrees with the experimental finding that the catalytic maximum occurs at equimolar concentrations of bromine and iodine bromide.

Taking into account eqn. (12), in which bromine and iodine are produced in equal amounts from iodine bromide, the concentration of bromine is given by $[IBr]\sqrt{K}$. Insertion of this expression for bromine in eqn. (25) leads to

$$d[C_6H_4Br{\cdot}OH]/dt = (kK'\sqrt{K})\,[C_6H_5{\cdot}OH][IBr]^2 \quad . \quad . \quad . \quad . \quad (26)$$

which accounts for the over-all kinetic order of three, one for phenol and two for iodine bromide.

The observed activation energy of this reaction at 0—10° (3·44 kcal. mole^{-1}) is almost identical with the true activation energy of the phenol–bromine reaction (3·24 kcal. mole^{-1}), and may therefore be assumed to be the true activation energy in the present case. On the other hand, the negative activation energy, −18·46 kcal. mole^{-1}, observed between 30° and 40° is the sum of the heat of dissociation of two moles of iodine bromide [eqn. (12)], the heat of formation of the phenol–bromine complex [eqn. (20)], and the activation energy, just deduced, of the rate-determining step [eqn. (19)]. Hence :

$$-18{\cdot}46 \text{ (obs. } E) = 3{\cdot}44 \text{ (true } E) - 27{\cdot}61\ (\Delta H \text{ of formation of the complex}) + 2\Delta H \text{ (dissocn. of IBr)} \quad . \quad . \quad (27)$$

from which ΔH (heat of dissociation of IBr) is 2·86 kcal. mole^{-1}. The substantial agreement of this value with that deduced from vapour-pressure data [8] (1·63 kcal. mole^{-1}) may be regarded as providing some justification for the proposed mechanism.

Additional evidence for the mechanism is furnished by a consideration of the activation energy of the anisole–iodine bromide reaction, which is −8·89 kcal. mole^{-1} at 30—40°. Given the similarity of the kinetics of this reaction to that of phenol (cf. Experimental section), it is justifiable to ascribe the same activation energy to the rate-determining step in the two cases. It follows then that for the anisole–iodine bromide reaction, we have:

$$-8{\cdot}89 \text{ (obs. } E) = 3{\cdot}44 \text{ (true } E) + \Delta H \text{ (heat of formn. of anisole–bromine complex)} + 2 \times 2{\cdot}86 \text{ (heat of dissocn. of IBr)} \quad . \quad . \quad . \quad . \quad . \quad (29)$$

so that ΔH is −18·05 kcal. mole^{-1}. This is less than the value for phenol–bromine complex (−27·61 kcal. mole^{-1}), as it should be since anisole is less reactive than phenol in bromination; the rate constant for 2% reaction at 30° for phenol is 77·36 and for anisole 0·90 l.^{2} mole^{-2} sec.$^{-1}$.

The authors thank R. Ganesan for some of the preliminary experiments.

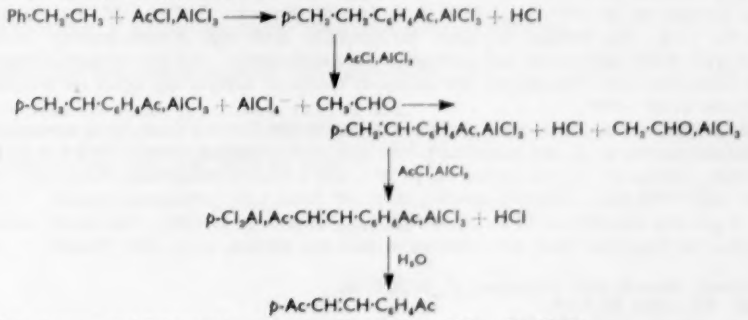
LOYOLA COLLEGE, MADRAS, INDIA. [*Received, May 31st,* 1956.]

960. *The Interaction of Alkylbenzenes with Excess of Friedel–Crafts Acetylating Agent.*

By G. BADDELEY and E. WRENCH.

This reaction, in methylene chloride, at 20° gives mainly *p*-alkylacetophenones. After removal of the solvent under reduced pressure, raising the temperature of the reaction mixture to about 70° effects further reaction, including dehydrogenation of the alkyl substituent and acetylation of the resulting styrene derivative.

ARYL KETONES having bulky *oo'*-substituents, *e.g.*, methyl groups, can be acylated by the Friedel–Crafts method; thus mesitylene and durene can be diacylated. Further, aromatic compounds such as *p*-ethylphenol and 5-*m*-xylenol, which have groups which greatly facilitate electrophilic substitution, readily undergo nuclear diacylation.[1] A different type of acylation of aromatic ketones is exemplified by the action of acetic anhydride–boron fluoride complex on acetophenone: acetoacetophenone is formed. On the other hand, acylation of alkylbenzene at room temperature and in the presence of aluminium chloride effects only monoacylation; further reaction occurs only at raised temperatures (about 70°) and may involve three or more competitive reactions: (i) The acylating agent may undergo self-condensation; thus an acetylating agent gives acetylacetone and other products. (ii) The aromatic component may be dealkylated; thus small amounts of acetophenone are among the products of the action of excess of acetylating agent on *p*-*n*-propyl- and *p*-*n*-butyl-acetophenone. (iii) The acetylating agent may dehydrogenate the alkyl substituent, giving an aldehyde and a styrene derivative which undergoes acylation of the ethylenic group; thus the action of excess of acetylating agent on ethylbenzene gives 4-*p*-acetylphenylbut-3-en-2-one:



[1] Von Auwers and Schornstein, *Fortschr. Chem. Phys.*, 1924—26, **18**, 76.

The reaction of excess of an acetylating agent with indane and tetralin has been reported;[2] we now describe its reaction with *m*-ethylacetophenone and a number of alkylbenzenes.

The products and yields (±5%) are listed in the Table. Where the yields do not total 100, non-volatile material was also obtained. The structures of the olefinic diketones

Exp.	Reactant	Products	
1	$Ph{\cdot}CH_2{\cdot}CH_3$	p-$C_6H_4Ac{\cdot}C_3H_5$ (60%)	p-$C_6H_4Ac{\cdot}CH{:}CHAc$ (10%)
2	$Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$	p-$C_6H_4Ac{\cdot}C_3H_7$ (40%)	p-$C_6H_4Ac{\cdot}CH{:}CHMeAc$ (15%)
3	$Ph{\cdot}CHMe_2$	p-$C_6H_4Ac{\cdot}CHMe_2$ (70%)	p-$C_6H_4Ac{\cdot}CMe{:}CHAc$ (10%)
4	$Ph{\cdot}CH_2{\cdot}CH_2Et$	p-$C_6H_4Ac{\cdot}C_5H_{10}$ (55%)	p-$C_6H_4Ac{\cdot}CAc{:}CHEt$ (35%)
5	Ph·CHMeEt	p-$C_6H_4Ac{\cdot}CHMeEt$ (30%)	p-$C_6H_4Ac{\cdot}CMe{:}CMeAc$ (25%)
6	$Ph{\cdot}CH_2{\cdot}CHMe_2$	p-$C_6H_4Ac{\cdot}CH_2{\cdot}CHMe_2$ (50%)	p-$C_6H_4Ac{\cdot}CAc{:}CMe_2$ (15%)
7	m-$C_6H_4Ac{\cdot}C_3H_5$	m-$C_6H_4Ac{\cdot}C_3H_5$ (60%)	m-$C_6H_4Ac{\cdot}CH{:}CHAc$ (30%)
	PhR (R = H, Me, Bu^t)	p-$C_6H_4Ac{\cdot}R$ (70%)	

were determined by conventional methods. In experiments 1, 2, 3, 5, and 7 the acetylphenyl group was sufficiently polarisable, even though its acetyl group was in combination with aluminium chloride, to provide an electromeric release of electrons which enabled acetylation to occur at the terminal carbon atom of the styrene system. Acetylation at the carbon atom adjacent to the ring occurred in experiments 4 and 6.

Experimental

Procedure.—Alkylbenzene was added to a cooled mixture of aluminium chloride (5 mols.) and acetyl chloride (3 mols.) in methylene chloride. When the ready reaction providing hydrogen chloride and 4-alkylphenyl methyl ketone had subsided the solvent was volatilised under reduced pressure and the temperature of the residue was raised until further reaction occurred. When evolution of hydrogen chloride was essentially complete, the mixture was decomposed with ice and dilute hydrochloric acid, and the organic product was extracted with chloroform, dried (K_2CO_3), and fractionally distilled under reduced pressure.

(i) *Ethylbenzene.* This (20 g.), after reaction at 110° for 2 hours, gave 4-ethylacetophenone (17·5 g.) (semicarbazone m. p. and mixed m. p. 153—154°), and 4-*p*-acetylphenylbut-3-en-2-one[3] (4 g.), b. p. 190—210°/15 mm. The latter crystallised from light petroleum in radiating needles, m. p. and mixed m. p. 107°, $\lambda_{max.}$ 2950 Å (ε 29,500). It gave: (*a*) terephthalic acid, m. p. 210° (dimethyl ester, m. p. and mixed m. p. 92°), on oxidation with dilute nitric acid (*d* 1·2) at 180°; (*b*) *p*-acetylbenzoic acid,[3] m. p. 205° (methyl ester,[4] m. p. 92°; 2 : 4-dinitrophenylhydrazone, m. p. 278°), on oxidation with aqueous permanganate at 0°; and (*c*) 4-*p*-acetylphenylbutan-2-one, m. p. and mixed m. p. 28°, on catalytic hydrogenation.

(ii) n-*Propylbenzene.* This (36 g.), similarly treated, gave 4-*n*-propylacetophenone (20 g.), b. p. 84—88°/0·5 mm. (oxime, m. p. and mixed m. p. 43—44°), and 4-*p*-acetylphenyl-3-methylbut-3-en-2-one (8 g.), b. p. 135—145°/0·5 mm. The latter was purified *via* its *disemicarbazone*, needles, m. p. 274—275° (decomp.) (from dilute acetic acid) (Found: C, 57·4; H, 6·2; N, 26·6. $C_{15}H_{20}O_2N_6$ requires C, 57·0; H, 6·3; N, 26·6%), and separated from light petroleum in radiating needles, m. p. 120°, $\lambda_{max.}$ 2900 Å (ε 34,520) (Found: C, 77·0; H, 6·9. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%). It gave terephthalic acid and *p*-acetylbenzoic acid by oxidation with dilute nitric acid and permanganate respectively. 4-*p*-Acetylphenyl-3-methylbut-3-en-2-one was also obtained by the action of excess of acetylating agent on 4-*n*-propylacetophenone at 90—100°.

(iii) iso*Propylbenzene.* This (80 g.), after reaction at 60—70° for 2 hr., gave acetophenone (1 g.) (semicarbazone, m. p. and mixed m. p. 202°), 4-*iso*propylacetophenone (74 g.), b. p. 120—125°/12 mm. (oxime, m. p. and mixed m. p. 70°), and 4-p-*acetylphenyl-pent-3-en-2-one* 10 g.), b. p. 117—120°/0·02 mm., radiating needles, m. p. 56° (from light petroleum) (Found: C, 77·6; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%), $\lambda_{max.}$ 2850 Å (ε 13,720). The *bis*-2 : 4-*dinitrophenylhydrazone* separated from nitrobenzene in dark red needles, m. p. 276° (Found: C, 53·3;

[2] Baddeley, Wrench, and Williamson, *J.*, 1953, 2110.
[3] Ingle, *Ber.*, 1894, **27**, 2507.
[4] Meyer, *Annalen*, 1883, **219**, 264.

H, 3·7; N, 19·5. $C_{25}H_{32}O_8N_8$ requires C, 53·3; H, 3·9; N, 19·9%). Oxidation of the pentenone with permanganate at 0° gave *p*-diacetylbenzene,[5] m. p. 114° (dioxime,[5] m. p. 248—250°); oxidation with dilute nitric acid gave terephthalic acid.

(iv) n-*Butylbenzene*. This (23 g.), after reaction at 80° for 6 hr., gave 4-*n*-butylacetophenone (17 g.), b. p. 140—146°/12 mm. (semicarbazone,[6] m. p. and mixed m. p. 185°), and a fraction, b. p. 145—165°/0·5 mm. (13 g.), which gave a solid which crystallised from light petroleum in *needles*, m. p. 152° (Found: C, 77·8; H, 7·0. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%), $\lambda_{max.}$ 2500 and 2900 Å (ε 9740 and 9300 respectively), which is probably 3-*p*-acetylphenylhex-3-en-2-one. It gave terephthalic acid and *p*-acetylbenzoic acid when oxidised with dilute nitric acid and permanganate respectively. Ozonolysis in a mixture of acetic acid and ethyl acetate at 0° gave propionaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 155°), and alkali-insoluble material, m. p. 112°, which gave *p*-acetylbenzoic acid by permanganate oxidation.

(v) sec.-*Butylbenzene*. This (26 g.), after reaction at 70° for 5 hr., gave 4-*sec.*-butylacetophenone (10 g.), b. p. 134—136°/14 mm. (semicarbazone,[7] m. p. and mixed m. p. 190°), and 4-p-*acetylphenyl*-3-*methylpent*-3-*en*-2-*one* (10 g.), b. p. 140—150°/0·2 mm., radiating needles, m. p. 162° (from light petroleum) (Found: C, 77·6; H, 7·3. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·4%), $\lambda_{max.}$ 2500 and 3000 Å (ε 21,900 and 15,540 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 180° (decomp.) (from nitrobenzene) (Found: C, 54·0; H, 4·1; N, 19·5. $C_{26}H_{24}O_8N_8$ requires C, 54·2; H, 4·2; N, 19·4%)]. Oxidation of the pentenone with dilute nitric acid and permanganate gave terephthalic acid and *p*-diacetylbenzene respectively.

(vi) iso*Butylbenzene*. This (53 g.), after reaction at 60° for 5 hr., gave 4-*iso*butylacetophenone (36 g.), b. p. 86—90°/0·5 mm. [*semicarbazone*, m. p. 206° (Found: C, 66·5; H, 8·2; N, 18·1. $C_{13}H_{19}ON_3$ requires C, 66·7; H, 8·2; N, 18·0%)], and a pale-green oil (12 g.), b. p. 120—135°/0·03 mm., which slowly darkened in the air. This oil in ethanol at 0° gave mainly 3-p-*acetylphenyl*-4-*methylpent*-3-*en*-2-*one* as a solid which separated from light petroleum in pale yellow needles, m. p. 159—160° (Found: C, 77·4; H, 7·5%), $\lambda_{max.}$ 2500 and 2950 Å (ε 23,740 and 17,520 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 190° (decomp.) (Found: C, 54·3; H, 4·7; N, 19·7%)]. This pentenone gave terephthalic acid on oxidation with dilute nitric acid, and *p*-acetylbenzoic acid and acetone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 128°), on oxidation with permanganate.

(vii) m-*Ethylacetophenone and excess of acetylating agent*. Acetyl chloride (32 g.) and 3-ethylacetophenone (28 g.) were added gradually to a cooled suspension of finely powdered aluminium chloride (84 g.) in methylene chloride (100 c.c.). The solvent was volatilised under reduced pressure and the residue was heated at 80° for 2 hr. The mixture was decomposed with ice and dilute hydrochloric acid and gave (i) 3-ethylacetophenone (16 g.), b. p. 117—119°/16 mm. (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 146°), and (ii) 4-m-*acetylphenyl*-*but*-3-*en*-2-*one* (20 g.), b. p. 120—130°/0·1 mm., needles, m. p. 76° (from light petroleum) (Found: C, 76·4; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·5%), $\lambda_{max.}$ 2450 and 2800 Å (ε 16,440 and 16,700 respectively) [*bis*-2 : 4-*dinitrophenylhydrazone*, m. p. 230° (Found: C, 52·5; H, 3·5; N, 20·1. $C_{24}H_{20}O_8N_8$ requires C, 52·6; H, 3·7; N, 20·4%)]. The butenone gave *iso*phthalic acid (dimethyl ester, m. p. and mixed m. p. 68°) on oxidation with dilute nitric acid, and *m*-acetylbenzoic acid,[8] m. p. 174° (Found: C, 65·7; H, 5·1. Calc. for $C_9H_8O_3$: C, 65·9; H, 4·9%), on oxidation with permanganate.

We thank Dr. F. Liversedge for the ultraviolet absorption spectra.

MANCHESTER COLLEGE OF SCIENCE AND TECHNOLOGY. [*Received, July 19th*, 1956.]

[5] Behrend and Herns, *J. pr. Chem.*, 1906, **74**, 134.
[6] Kursanov and Zelvin, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 2173; *Chem. Abs.*, 1940, **34**, 4062.
[7] Hennion and McLeese, *J. Amer. Chem. Soc.*, 1942, **64**, 2421.
[8] Rupe and Mejewski, *Ber.*, 1900, **33**, 3408.

961. *Water-soluble Complexes of Niobium (Columbium) and Tantalum. Part I. Complexes with α-Hydroxy-acids and (2-Hydroxyethyl)-amines.*

By Fred Fairbrother and John B. Taylor.

The solubility of niobic acid and tantalic acid in the α-hydroxy-acids glycollic, lactic, malic, and citric has been studied and solid 1 : 1 complexes isolated. The complexes are only stable in aqueous solution in the presence of excess of α-hydroxy-acid. No dissolution was observed in solutions of the dibasic acids malonic, succinic, adipic, or phthalic.

The solubility was also studied in the (2-hydroxyethyl)amines (" ethanolamines ") and polynuclear species were isolated.

Pure tantalic acid is much less soluble than pure niobic acid in all these complex-forming agents. Even where the solubility ratio is very great, however, there is no satisfactory separation by differential solubility of the coprecipitated acids.

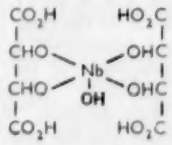
The insolubility of the oxides of niobium (columbium) [1] and tantalum [2] in all common acids were among the first properties of these elements to be observed. In the 150 years since their discovery, few water-soluble compounds other than the complex fluorides [3] have been reported, and these mostly only in solution. The only ones that have received any measure of systematic examination have been the complexes with oxalic and tartaric acids, and of the composition and manner of formation of these there still exists some doubt. So far, no water-soluble cationic species of these elements, simple or complex, has been discovered. Russ [4] in 1902 reported that hydrated niobium oxide was soluble in oxalic acid and claimed to have prepared a complex oxalate $Nb(HC_2O_4)_5$ by the dissolution of the hydrated oxide in an excess of oxalic acid and also, by the reaction of oxalic acid with alkali niobates, a series of crystalline salts of the empirical formula $Nb_2O_5,3M^1_2O,6C_2O_3,xH_2O$. This formula would correspond to $M^1_3[Nb(C_2O_4)_3O],xH_2O$ implying a niobium co-ordination number of 7 but could equally well be written $M^1_3[Nb(C_2O_4)_3(OH)_2],(x-1)H_2O$ with a more symmetrical co-ordination number of eight.

In an appendix Russ stated that an attempt to prepare the corresponding oxalate–tantalum salts led to precipitation of the hydroxide, and solutions containing $Ta_2O_5,5M_2O,10C_2O_3$. The oxalate complex of tantalic acids was also found to be more easily decomposed by weak bases. Britton and Robinson [5] carried out conductometric and potentiometric titrations of alkali niobate and tantalate solutions with acids chosen chiefly for their varying strengths and found that, whilst strong and moderately strong acids precipitated the hydroxides readily, oxalic, lactic, tartaric, and malic acids retained the oxides in solution. They concluded from their experimental results that lactic acid does not appear to form complex lacto-niobic or -tantalic acids and that complex formation, as shown by the ability to hold these relatively insoluble oxides in clear solutions, is not confined to hydroxy-acids. In this connection oxalic acid was mentioned as a non-hydroxy-acid " in which the dissolution is probably of a colloidal nature." We shall show later that it is just this property of behaving as a hydroxy-acid which gives to oxalic acid its strong complex-forming power, and that the solutions therein of the hydroxides are not colloidal.

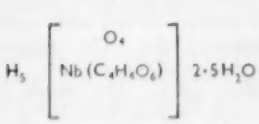
Edminster and Albritton,[6] by evaporation of a solution of freshly precipitated niobium hydroxide in tartaric acid, claimed to have obtained a crystalline compound $(C_4H_4O_6)_2NbOH$, *i.e.*, with two molecules of tartaric acid associated with each niobium atom, to which they ascribed the formula (I), the niobium having its normal co-valency of five. Such a formula would imply four replaceable hydrogen atoms.

[1] Hatchett, *Phil. Trans.* 1802, 49.
[2] Ekeberg, *Svensk Vet. Akad. Handl.*, 1802, **23**, 180.
[3] Marignac, *Ann. Chim. Phys.*, 1866, **8**, 5.
[4] Russ, *Z. anorg. Chem.*, 1902, **31**, 49.
[5] Britton and Robinson, *J.*, 1933, 419.
[6] Edmister and Albritton, *J. Amer. Chem. Soc.*, 1932, **54**, 438.

Srinivasan [7] systematically investigated tartratoniobic acid and obtained from a solution of niobic acid in tartaric acid, by precipitation with alcohol, a microcrystalline precipitate with the composition $Nb_2O_5(C_4H_4O_5)_2.10H_2O$, *i.e.*, with *one* tartaric acid molecule associated with each niobium atom, and to which he attributed a heteropoly-acid structure (II), although only one hydrogen atom in the molecule was replaceable by an alkali metal. Thus, a number of alkali salts of a tartaric–niobic acid complex, of the general formula $M^I_2O,Nb_2O_5(C_4H_4O_5)_2,xH_2O$, were prepared by the dissolution of the alkali niobate in tartaric acid.[8] Several salts of bivalent cations were also prepared by double decomposition of the potassium salt of this complex with the appropriate metal salt.[9] In all of these, only one hydrogen of the above formula was replaced.



(I)



(II)

Evidence of complex formation in solution between niobium hydroxide and citric, malic, lactic, gluconic, and tartronic acids is also given by the polarographic reduction of niobium in the presence of these acids.[10]

We have now examined the preparation, composition, and reactions of a number of water-soluble complexes of niobium, in a variety of α-hydroxy-acids and -amines. From the outset it may be stated that the work relates principally to the preparation of niobium complexes, since *pure* tantalic acid is markedly less soluble than *pure* niobic acid in all the complex-forming agents examined, and such complexes of tantalum as are formed are more easily decomposed. In this work we shall for brevity retain the names niobic or tantalic acid, respectively, for the hydrated oxides, although their acidic nature only becomes evident upon fusion with an alkali.

Experimental

Niobic and tantalic acids were prepared in batches by fusing 1—2 g. of the pentoxide (>99·9% purity) or alternatively in the case of niobium also the metal powder, with 5—10 g. of potassium pyrosulphate. The clear melt was cooled and dissolved with stirring in boiling 25% oxalic acid solution. The solution was filtered to remove insoluble matter, 2—3 g. of ammonium chloride were added and then 4N-ammonia solution, dropwise to the boiling solution, until precipitation was complete. Further ammonia was added until the pH was about 10. The heavy white precipitate, which settled rapidly on standing, was centrifuged hot, to avoid crystallisation of ammonium oxalate, washed five times on the centrifuge with about 3% ammonium chloride solution and then twice with hot distilled water.

Removal of the soluble salts by washing with water alone is, in the case of niobic acid, quite impracticable. As the washing proceeds the acid becomes more colloidal, so that centrifuging for 2 hr. at a relative centrifugal force value of 3000 may be insufficient to give a clear supernatant liquid. This tendency towards peptisation of the acid on washing is characteristic of the product of precipitation by the addition of ammonia solution to an acid oxalate solution. An alternative method of preparation, fusion of the pentoxide with alkali followed by decomposition of the niobate with mineral acid, gives a product which is much more granular and less easily peptised, but which is also less reactive towards complex-forming agents. Tantalic acid, in contrast to niobic acid, showed no tendency to peptisation on washing and gave a granular, relatively unreactive precipitate by whichever method it was prepared.

The reactivity of niobic acid towards complex-forming agents also varied greatly with its age. Freshly precipitated niobic acid prepared as described is the most reactive but the

[7] Srinivasan, *Proc. Indian Acad. Sci.*, 1950, **31**, 194.
[8] *Idem, ibid.*, p. 300.
[9] *Idem, ibid.*, p. 381.
[10] Ferrett and Milner, A.E.R.E., C/R 1752, 1955.

reactivity rapidly falls on standing, even overnight, so that eventually it becomes comparable with that of niobic acid obtained by acidification of a niobate.

Solubility of Tantalic Acid.—Since tantalic acid showed no obvious tendency towards colloidality, attempts were made to measure its solubility in water by tracer methods. 0·231 g. of a mixed sodium potassium tantalate containing 0·1007 g. tantalum was neutron-irradiated in a Polythene tube until it had an activity of about 2·5 mc. of ^{182}Ta. After irradiation the contents of the tube were dissolved in 200 c.c. of distilled water and the tantalic acid precipitated by the addition of 10% perchloric acid to the hot solution. To reduce the possibility of adsorption of the activity on the glass surfaces, all vessels were treated with Silicone resin (Imperial Chemical Industries R.230 applied in 1% xylene solution and cured at 150—200°).

The precipitated tantalic acid was well washed on the centrifuge and shaken in a thermostat at 25° with de-ionised water for 15 days. At intervals of 4, 7, 8, 9, 10, 11, and 15 days samples of the suspension were withdrawn and centrifuged and 10 c.c. of the clear liquid evaporated on a small planchet by infrared light. The radioactivity was determined in the usual way with a G.E.C. EHM2 thin mica-window counter. The reproducibility of the assay was carefully checked and was within ±4%. The results of the "solubility" measurements, however, were quite unreproducible, varying from 10^{-6} g. of Ta/100 c.c. to zero. Moreover, the greater the centrifugal force and the time of centrifuging, the smaller was the activity left in the liquid phase. One must conclude therefore that tantalic acid in pure water is, like niobic acid, also a colloid. This conclusion was confirmed by centrifuging a sample of the suspension for a short time to remove the larger particles and placing it in a "Kalle" dialysis tube. After 6 days no activity had diffused through the membrane, which readily passed such ions as $[(NH_3)_5ClCo]^{2+}$ and $[(NH_3)_6Co]^{3+}$.

In view of the fact that niobic acid passes even more easily into the colloidal state and indeed has been shown to be a radio-colloid [11] it is very unlikely that any "solubility" measurements in water of niobic acid would have much significance.

Preparation of the Complexes.—The same general method was used for all the complexes now described, with individual variations noted below. As a preliminary exploration, samples of niobic or tantalic acid were refluxed for 24 hr. with a fairly concentrated aqueous solution of the carboxylic acid under review, the suspension was cooled and centrifuged, and the clear liquid tested for the presence of niobium or tantalum by the tannin reaction. In cases where reaction occurred an amount of the freshly precipitated niobic or tantalic acid, containing about 1 g. of the metal, was refluxed for about 24 hr. with a 2—3% solution of the carboxylic acid, sufficient to dissolve the whole of the earth acid had reaction been complete. In practice, however, rarely more than one-third of the niobic acid, and only traces of pure tantalic acid, dissolved. Hardly any dissolution occurred in the cold. Previous workers have reported that a considerable excess of oxalic acid is required to dissolve niobic acid completely. It was found that in the case of the weaker complex-forming agents, glycollic and lactic acid, the continuous addition of ammonia so as to maintain the pH at 8—9 greatly increased the rate of dissolution of niobic acid. This clearly points to the α-hydroxy-acid anion being the effective complex-forming agent. After removal of undissolved hydroxide by centrifuging, the clear liquid was evaporated to a syrup under reduced pressure at 60° and the complex precipitated by the addition of an alcohol–ether mixture of a composition that would dissolve any uncombined hydroxy-acid. In this way the glycollic, lactic, malic, citric, and tartaric α-hydroxy-acids were found to form, with niobic acid, solid water-soluble complexes of definite composition. The precipitated acids were all non-crystalline and only gave very diffuse *X*-ray powder diagrams. They were so soluble in water that solubility measurements were impracticable with the amounts available, and attempts to crystallise by moistening or leaving in a moist atmosphere led, in the case of lactic, citric, and tartaric acids to the formation of straw-coloured hydrated scales which appeared crystalline but which in fact proved to be non-crystalline and glass-like.

All the solid α-hydroxy-acid complexes from which the excess of hydroxy-acid had been dissolved by the precipitant hydrolysed slowly on re-dissolution in water, this first becoming evident by a gradual clouding of the solution. It appears that α-hydroxy-acid complexes of niobic acid are only stable in the presence of an excess of complex-forming agent, usually at least three-fold but often much greater. There is much evidence for this. If a solution of an α-hydroxy-acid complex be placed in a dialysis tube suspended in running water, some niobic acid diffuses through as complex but most remains and is gradually precipitated as the hydroxy-acid is removed; a greater fraction of the niobium content can be dialysed away if

[11] Schubert and Conn, *Nucleonics*, 1949, **4**, No. 6, 2; Schubert and Richter, *J. Colloid Sci.*, 1950, **5**, 376.

more complex-forming agent be added. In the same connection it was observed that sodium niobate, crystallised from alkaline solution, was hydrolysed with precipitation of niobic acid in a dialysis tube. This is in agreement with Hauser and Lewite's [13] observation that alkali niobate solutions can be dialysed through parchment membranes, yielding a stable niobium pentoxide sol practically free from alkali. Similarly, transport experiments with all complexes showed a net migration of niobic acid (as complex) to the anode with also, in the case of solutions containing more than about 1·5 g. of complex in 100 c.c., a precipitation of niobic acid gel at the cathode. In all preparations of the complexes, even after long refluxing the solution contained both excess of niobic acid and also free hydroxy-acid. The beginning of hydrolysis was not apparent to the eye and could only be followed quantitatively by a light-scattering photometer. Solutions which were clear to the eye gave a strong Tyndall scattering. It is to this sol formation that many of the conflicting statements in the literature are due. Clear solutions of many of the present α-hydroxy-complexes were precipitated on boiling by the addition of a neutral salt, *e.g.*, potassium chloride.

Reactions.—The complexes gave the usual tannin precipitate, were decomposed with precipitation of niobic acid by cold 3N-sulphuric, -hydrochloric, or -nitric acid and 3N-sodium hydroxide, and by boiling 3N-acetic acid. Decomposition by hot 3N-sodium hydroxide gave, on cooling, crystals of the sparingly soluble sodium niobate.

Analysis.—The quantitative estimation of either niobium or tantalum in the absence of the other is relatively simple and a variety of gravimetric techniques are available, the metal usually being weighed as the ignited pentoxide. Niobic acid in the complexes now described was estimated partly by ignition of the tannin precipitates and partly by ashing and ignition of the compound itself.

Since, however, it was desired to investigate the possibility of using the differences in stabilities of the niobium and tantalum complexes as a means of separation, it was also necessary to explore the methods of estimating these two metals in the presence of one another. The difficulty of this has been commented upon by all who have worked in this field. Methods which have been used include fractional precipitation of the tannin complexes,[13] chromatography,[14] polarography,[15] *X*-ray fluorescence,[16] and colorimetry.[17] The chief difficulty of precipitation methods, as will be discussed further, lies in the fact that these elements lose much of their individuality when present together, and no precipitant yet known will clearly precipitate one without the other; at best, fractional precipitation becomes necessary.

In the present work, in addition to the gravimetric methods mentioned, niobium was estimated colorimetrically by the intensity in concentrated hydrochloric acid of the absorption peak at 282 mμ.[18] Control estimations by gravimetric methods showed this to be a rapid and reliable method and free from serious interference by tantalum, which also appears to form a complex with hydrochloric acid, with an absorption peak at 271 mμ. The optical density of the tantalum complex, however, is only about one-tenth that of the niobium complex in equivalent concentrations. Both complexes are destroyed by dilution with water or by boiling the concentrated acid solution.

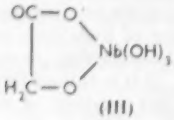
Tantalum and niobium were also determined together by the pyrogallol colorimetric method [19] and thence tantalum by difference.

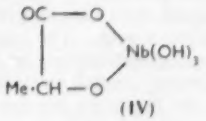
Perhaps the most direct method of estimating one of these metals when both are present, and which in this work proved the lack of separation from a mixed precipitate, was the use of radio-niobium and -tantalum. Tantalum-182 was obtained as already described. Niobium-95 (35 d.) was obtained as a carrier-free separated uranium-fission product in the form of the niobic acid–oxalate complex. This was radiochemically purified by dilution with a known weight of inactive niobic acid in oxalic acid solution, the oxalate complex destroyed by fuming with mixed perchloric and sulphuric acids under an infrared lamp, and the niobic acid re-precipitated with lithium hydroxide. During this work the previous observation [6] that niobic acid

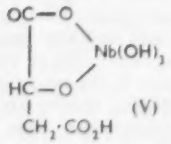
[13] Hauser and Lewite, *Z. angew. Chem.*, 1912, **25**, 100.
[13] Schoeller and Powell, "Analytical Chemistry of Tantalum and Niobium," Chapman and Hall, London, 1937.
[14] Burstall, Swain, Williams, and Wood, *J.*, 1952, 1497.
[15] Elving and Olson, *Analyt. Chem.*, 1956, **28**, 338, and ref. 10.
[16] Campbell and Carl, *Analyt. Chem.*, 1954, **26**, 800; 1956, **28**, 960; Mortimac, Romans, and Tews, *Appl. Spectroscopy*, 1954, **8**, 24.
[17] Geld and Carroll, *Analyt. Chem.*, 1949, **21**, 1098; Telep and Boltz, *ibid.*, 1952, **24**, 163; Freund and Levitt, *ibid.*, 1951, **23**, 1813; Lauw-Zecha, Lord, and Hume, *ibid.*, 1952, **24**, 1169. See also refs. 18, 19, and 21.
[18] Kanzelmeyer and Freund, *Analyt. Chem.*, 1953, **25**, 1807.
[19] Dinnin, *ibid.*, p. 1803.

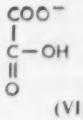
is not quantitatively precipitated from its oxalate solution by ammonia was confirmed. Mixtures of ^{182}Ta and inactive niobium or of ^{95}Nb and inactive tantalum enabled unambiguous determinations to be made of the composition of a precipitate.

Complexes of Niobic Acid.—Glycollic acid. The crude product precipitated from a solution of niobic acid in ammonium glycollate contained ammonium ion. This was removed by passing the solution through a column of Amberlite-120 (H) in the acid cycle which removed


(III)


(IV)


(V)


(VI)

the ammonium ion without decomposing the complex. The resulting solution, after concentration at 50—60° under reduced pressure gave a heavy white precipitate of the 1 : 1 glycollic–niobic acid *complex* (III). This was washed with ether and dried in a vacuum (Found : C, 11·0; Nb, 41·2%; C : Nb, 2·06 : 1. $C_2H_3O_4Nb$ requires C, 11·0; Nb, 42·7%; C : Nb, 2 : 1).

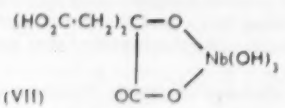
Thioglycollic acid. Sulphur-containing chelate rings are usually very stable, and thioglycollic acid forms stable chelates with several transition elements. This reagent or its ammonium salt, however, failed to dissolve niobic acid appreciably under conditions where the hydroxy-acid readily formed a complex. This is additional evidence of the importance of the hydroxyl group in the formation of the present series of complexes.

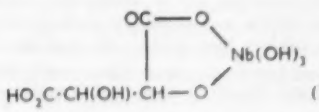
Lactic acid. Prepared and purified as described for glycollic acid, the *complex* (IV) in aqueous solution readily passed through a dialysis membrane [Found : C, 15·5; Nb, 40·9%; C : N, 2·94 : 1; *M* (cryoscopic, mean), 240. $C_3H_7O_6Nb$ requires C, 15·6; Nb, 40·3%; C : N, 2 : 1; *M*, 232].

Malic acid. Niobic acid was warmed to about 95° with a large excess of a solution of *rac.*-malic acid. In a few hours it almost completely dissolved. From the clear solution ether–alcohol precipitated a *complex* (V) of similar reactions to those described (Found : C, 17·5; Nb, 31·4%; C : Nb, 4·25 : 1. $C_4H_7O_8Nb$ requires C, 17·5; Nb, 33·8%; C : Nb, 4 : 1). It may be noted that the substance precipitated was a 1 : 1 complex although a large excess of hydroxy-acid was present. The complex was acid in reaction as would be expected from the presence of an uncomplexed carboxyl group.

Oxalic acid. Russ [4] prepared the oxalate complex by dissolving niobic acid in a large excess of oxalic acid from which he separated it by fractional crystallisation and obtained an oxalate : niobium ratio of 5 to 1. We refluxed an excess of niobic acid in 1·2 g. of oxalic acid and 70 c.c. of water for 20 hr. The amounts of niobic acid dissolved [as $Nb(OH)_5$] were 0·48 g., 0·39 g., and 0·56 g. in three experiments with different samples, the variation being due to differences in reactivity of the samples. Careful evaporation of one of these solutions over phosphoric oxide at room temperature gave a white amorphous powder with an oxalate : niobium ratio of 2·8 : 1 which is probably the parent acid of Russ's salts. It is unstable and on re-dissolution in water gradually precipitates niobic acid.

The oxalate complexes diffuse through a dialysis membrane. The solutions therefore are not collodial in character, but become so if the complex is decomposed by dilute acid or alkali, even though, as may happen in the cold and at low ionic strengths, a considerable time may elapse before visible flocculation occurs.


(VII)


(VIII)

Oxalic acid is exceptional among the acids now discussed also in other ways. In the first place it is not obviously an α-hydroxy acid. It is, however, a fairly strong acid ($K_1^{25} = 6{\cdot}5 \times 10^{-2}$) so that in acid solution there is always an appreciable amount of the anion $HC_2O_4^-$ present which can be regarded as an α-hydroxy-anion (VI) which almost certainly behaves as the other α-hydroxy-anion groups.

Citric acid. The white *complex* (VII) was precipitated by alcohol–ether (Found : C, 20·3; Nb, 27·4%; C : Nb, 5·8 : 1; *M* (cryoscopic in water), 337. $C_6H_9O_{10}Nb$ requires C, 21·2; Nb,

27·4%; C : Nb, 6 : 1; *M*, 340). It is almost certain that only the central carboxyl group is involved in complex formation since inclusion of either of the terminal groups would require the formation of a 6-membered ring which the present work has shown to be unstable.

Transport experiments showed a migration of the niobium to the anode.

In view of the two uncomplexed carboxyl groups, it was thought that it should be possible to prepare salts of this complex by direct neutralisation. This aspect of the problem has not been fully explored. Hot sodium hydroxide solution decomposes the complex, depositing crystals of the sparingly soluble sodium niobate on cooling.

Tartaric acid. The complex formed between niobic acid and tartaric acid has already received much attention. The composition has been described both as a 1 : 1 and 1 : 2 complex. We prepared the complex (VIII) by the general methods described above, and isolated it by precipitation with alcohol (Found : C, 13·9; Nb, 31·5%; C : Nb, 3·5 : 1. Calc. for $C_4H_7O_9Nb$: C, 16·4; Nb, 31·8%; C : Nb, 4 : 1).

Discussion

In contrast to the foregoing results, no dissolution of niobic acid was found to occur with the dibasic acids malonic, succinic, adipic, or phthalic, or with potassium hydrogen phthalate, and of the acid ammonium salts only in the case of malonic acid and that to a barely detectable extent. Similarly the amounts dissolved by sodium β-hydroxybutyrate or thenoyltrifluoroacetone in benzene, water, or alcohol solution or by acetylacetone in alcohol or water were so small as to leave some uncertainty as to whether they were in true solution.

The results leave no doubt that the present series of α-hydroxy-acid niobium complexes are formed by the co-ordination of the acid anion to the niobium and the completion of a five-membered ring by elimination of water.

Since the niobic acid as such is invariably present as a hydrated suspension or a colloid, whether as a starting material or as the product of decomposition, it is more profitable to regard the formation of these complexes as heterogeneous reactions. Throughout, we have found that rate processes and the history or mode of preparation of the earth acid are of more significance than ionic equilibria involving complex niobium species. The effect of rapid ageing on the reactivity of the precipitated niobic acid has already been noted. Many of the conflicting statements in the literature regarding non-precipitation by various reagents can be attributed to hysteresis. Attempts were made to accelerate the attainment of a steady state (" equilibrium " would be incorrect since this would imply the possibility of approach from either side) by ultrasonic radiation at a frequency of 1 megacycle/sec. and a power of 250 w. The results were disappointing. The solutions became heated but the rate of reaction was no greater than that produced by boiling.

The coagulation, precipitation, or dissolution of niobic or tantalic acids appears to take place through a reversible condensation of neighbouring hydroxyl groups, whether of adjacent earth acid units or of earth acid and a complex-forming agent. For the latter, either two hydroxyl groups, or one hydroxy-group and a carboxylic anion, in the α-position are necessary to make possible the formation of a 5-membered chelate ring. Examples of the condensation involving two hydroxyl groups are given by the catechol complexes.[20]

The actual process of dissolution can be visualised as the attachment of a molecule of complex-forming agent in this way to one of the peripheral hydrated niobium atoms of a particle or colloid micelle, with the subsequent breaking of the metal–oxygen bonds which hold it to the rest of the particle. The lower solubility of tantalic acid must be attributed to the greater stability of the Ta–O–Ta bonds relative to the stability of the complexes.

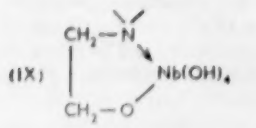
Experience with malonic and β-hydroxybutyric acids indicates that six-membered rings, though not impossible, are much less stable. This is not surprising, for the *average* bond angle in a five-membered ring is 108° compared with 120° in a six-membered ring. Since the Nb–O bonds are probably largely covalent the smaller ring would involve much less strain.

[20] Rosenheim and Roehrich, *Z. anorg. Chem.*, 1932, **204**, 342.

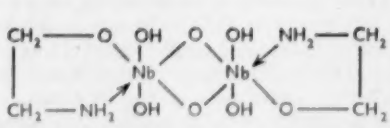
It appears, however, that six-membered rings can be formed in solution with strong inorganic polyhydroxy-acids. Niobic acid is also appreciably soluble in chromic and ortho- and poly-phosphoric acids, all of which form oxygen-bridged condensed acids with hydroxyl groups in the required position, and also, as is well known, in concentrated sulphuric acid. The last, in conjunction with alkali pyrosulphate fusion, has long been the principal reagent for the dissolution of niobic or tantalic oxides. Freshly precipitated and centrifuged, but still moist, niobic or tantalic acid will dissolve slowly in 10% oleum from which, as from the product of pyrosulphate fusion, it is precipitated on dilution with water and boiling. The dissolution probably occurs through chelation with the disulphuric (pyrosulphuric) anion, which is decomposed by water. The hysteresis in the precipitation of niobic acid from sulphuric acid solution is most marked. The solution can be diluted to about half-molar strength in the cold and only begins to become cloudy after 1—2 hr. On the other hand it is rapidly precipitated on boiling from a 5M-solution. Selenic acid is particularly interesting for comparison. Niobic acid dissolves rapidly to give a clear solution in 15M-selenic acid but is precipitated in the cold on dilution to about 7M, at which concentration it is not precipitated from sulphuric acid even on boiling.

It should be pointed out that although in the present series of α-hydroxy-acid complexes the molecular ratio of niobic to α-hydroxy-acid was, with the exception of oxalic acid, always 1 : 1, this does not entirely exclude the formation of complexes containing additional molecules of α-hydroxy-acid which might be removed by the alcohol or ether used as precipitant.

Following the foregoing results with α-hydroxy-acids and the observation—which will form the subject of a later communication—that niobic acid and, to a less extent tantalic acid, form water-soluble complexes with a variety of nitrogen bases, we also studied the complex-forming action of the (2-hydroxyethyl)amines ("ethanolamines"), since these contain both a hydroxyl group and a basic nitrogen atom in such a position that the formation of a five-membered chelate ring seemed possible (cf. IX).



(IX)



(X)

The only previous indication of the formation with niobium of a chelate ring of this type is that implied in the formation of a water-insoluble complex with 8-hydroxyquinoline.[21]

(2-Hydroxyethyl)amines used were commercial products and were fractionated under reduced pressure at least three times; they had b. p.: (2-hydroxyethyl)amine, 100°/53 mm.; di-(2-hydroxyethyl)amine, 160°/18 mm.; tri-(2-hydroxyethyl)amine, 210—212°/16 mm.

Complex formation was followed in the same way as for the α-hydroxy-acids. The three hydroxyethylamines showed a considerable difference both in rate and amount of dissolution, those in (2-hydroxyethyl)amine being the greatest and in tri-(2-hydroxyethyl)amine the least. For example, excess of freshly precipitated niobic acid, from the same preparation, was refluxed for 20 hr. under the same conditions with 70 c.c. of 0·0095M-solutions of each of the amines. This concentration was the same as used in the α-hydroxy-acid experiments and corresponds to a concentration of 2 g. of citric acid in 70 c.c. of water, which was found to be a convenient standard for comparison.

After removal of excess of solid by centrifuging, solid complexes were isolated by vacuum evaporation below 50° followed by alcohol–ether precipitation, or the "solubility" measured by evaporation to dryness and ignition. The amounts dissolved (g. per 100 c.c. of 0·0095M-amine) were as follows, the first figure in parentheses referring to Nb_2O_5, and the second to Ta_2O_5: (2-Hydroxyethyl)amine (0·148, 0·016); di-(2-hydroxyethyl)amine (0·104, 0·003); tri-(2-hydroxyethyl)amine (0·045, 0·004). Reaction is much the most extensive with the first amine. The weight of tantalic acid dissolved was in each case very much less than that of the niobic acid.

[21] Kasner, Garcia-Porrata, and Grove, *Analyt. Chem.*, 1955, **27**, 492.

The complexes were white powders, soluble in water except in the case of tri-(2-hydroxyethyl)amine where rapid hydrolysis gave an immediate cloudy solution : 3N-mineral acids and 3N-acetic acid precipitated niobic acid : 2N-ammonia solution had no effect. Sodium hydroxide gave the niobate as with the α-hydroxy-acid complexes.

Analysis and molecular weight determination pointed to no simple formula but rather to polynuclear species.

		Found :			Required :		
Amine	Formula	C (%)	Nb (%)	*M*	C (%)	Nb (%)	*M*
2-Hydroxyethylamine ...	$(HO{\cdot}C_2H_4{\cdot}NH_3)_3[Nb(OH)_4]_3$	10·8	45·9	430	11·8	45·8	406
Di(-2-hydroxyethyl)amine	$[(HO{\cdot}C_2H_4)NH_2]_3[Nb(OH)_4]_4$	11·2	47·6	880	12·2	47·7	796
Tri-(2-hydroxyethyl)amine	$[(HO{\cdot}C_2H_4)_3N]_2[Nb(OH)_4]_3$	14·0	45·0	—	13·9	44·9	1059

The formation of these complexes from niobic acid probably takes place in the same way as with α-hydroxy-acids, by the attachment of the ligand to the periphery of the hydrated particle followed by detachment of the complex from the parent micelle. In the case of the hydroxyethylamines the fragments detached appear to be larger than in the case of the hydroxy-acids. One possible structure for the mono-(2-hydroxyethyl)amine complex is (X) with similar structures for the di- and the tri-(2-hydroxyethyl)amine complex, containing respectively four and five niobium atoms bridged by oxygen atoms.

In all the foregoing experiments, the most outstanding feature was the much smaller solubility in solutions of all the complex-forming agents of freshly precipitated tantalic acid, than of niobic acid; even greater difference was found for dissolution by amines. In a solution of diethylamine almost 1000 times more niobic acid than tantalic acid was dissolved under the same conditions. In the hydroxyethylamines the ratio was only about 10 to 30 times and in citric acid about 50 times.

In view of these wide differences it was hoped that a satisfactory method of separation of the metals might be devised, based on their differential solubility, which would avoid the use of the hydrofluoric acid associated with the only successful commercial separations devised in 100 years. No satisfactory separation of the co-precipitated acids, however, has yet been achieved, owing to the fact that each of these two elements appears to lose its identity when intimately mixed with the other. This fact has been commented upon from various angles by several workers. In the present work niobic oxide and tantalic oxide in about equal proportions were (*a*) fused separately with pyrosulphate, dissolved in oxalic acid precipitated as the hydroxides washed and then mixed; (*b*) fused with pyrosulphate and dissolved in oxalic acid separately, but the hydroxides simultaneously precipitated from the mixed oxalic acid solutions; (*c*) mixed before fusion, etc. The products of (*a*), (*b*), and (*c*) were then treated in the same way with solutions of complex-forming agents. In (*a*) the niobic and tantalic acids behaved quite independently and very little tantalic acid passed into solution. In (*b*) and (*c*) no separation was achieved and far more tantalic acid passed into the aqueous phase that would have done so under the same experimental conditions but in the absence of niobic acid.

Many experiments were carried out along these lines but four will suffice to illustrate this point.

(*a*) Approximately equal weights of niobium pentoxide and tantalum pentoxide were converted into the hydroxides, mixed, and refluxed with a 5% solution of diethylamine in water for ¾ hr. The ratio Nb : Ta in the aqueous phase was 200 to 1. (*b*) A similar experiment but the oxides were first fused together : The ratio Nb : Ta in aqueous phase was 6·7 to 1. (*c*) With 2 g. citric acid in 70 c.c. water and a reflux time of 22 hr. the niobium extracted from separately precipitated mixed hydroxides contained less than 2% of tantalum, in close agreement with individual experiments on the separated oxides. (*d*) When the hydroxides were co-precipitated the niobium contained 16% of tantalum, whilst on doubling the citric acid concentration the tantalum content rose to 25%. This enhanced solubility of tantalic acid in the presence of niobic acid could be due to either or both of two causes : (i) a separation of the tantalum atoms and breaking of the strong Ta–O–Ta bonds in the mixed micelle (since it is neither solid nor crystalline, " solid solution " or " mixed crystal " seems inappropriate) in a somewhat similar manner to the increased speed of dissolution of some metals when alloyed, or (ii) the formation of polynuclear species in the aqueous phase.

We are of the opinion that the latter is probably the major cause of the observed effect. That it is not simply due to a greater slowness of dissolution of tantalic acid with the formation of a complex of comparable stability to that of niobium is shown by the fact that the reverse process, that of hydrolysis, takes place more readily with tantalum.

In the case of the present α-hydroxy-acid complexes, although freezing-point determinations gave values approximately those of the monomeric species, the precision was not sufficient to exclude polynuclear units. Moreover, although the solutions were clear, some hydrolysis undoubtedly occurred.

In the case of the hydroxyethylamines the evidence was much clearer that the oxides passed into the aqueous phase as polynuclear units. In such a unit the tantalic acid molecules can be condensed with niobic acid molecules as in the mixed micelle.

It follows therefore that it is unlikely that a successful separation process can be devised which does not involve the metals as single atoms unconnected through oxygen bonds or other bridges. The success of the separation processes involving the complex fluorides may be attributed to the monomeric character of these complexes.

We are indebted to the Department of Scientific and Industrial Research for a maintenance grant to one of us (J. B. T.).

MANCHESTER UNIVERSITY. [*Received, July 24th, 1956.*]

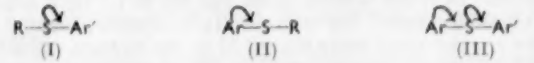
---

962. *Search for Spectral Evidence of Expansion of the Valency Shell of Sulphur in Aromatic Sulphides.*

By A. MANGINI and R. PASSERINI.

The possibility of spectral changes through the occurrence of a type of conjugation in which sulphur is the electron acceptor in systems *p*-X·C_6H_4·SR, where X = O^-, OH, NH_2, or NMe_2, has been examined. For this purpose the near-ultraviolet absorption spectra of some 30 aromatic sulphides or (for comparison) ethers have been traced, often in more than one solvent, and, in some cases in which acid or basic groups were present, at more than one pH. It is concluded that none of the observed spectral effects can be assigned with certainty to conjugation of the type considered. These results, together with parallel work on the dipole moments of aromatic sulphides, indicate that this form of conjugation, if operating, is not important in these systems.

WE have for some time been studying the spectral evidence of sulphur conjugation in aromatic sulphides. There are two basic types of possible conjugation. The best understood (I) involves inclusion of sulphur 3*p* electrons in an aryl π shell: evidence concerning it comes from the study of chemical equilibium,[1] dipole moments,[2] and spectra.[3] The other type (II) depends on incorporation of aryl π electrons into 3*d* sulphur orbitals, and we began our spectral study of this possible effect by considering its expected consequence that a combination of processes (I) and (II) in a diaryl sulphide should, as shown in (III), lead to conjugation between one aromatic ring and the other. The main



(I) (II) (III)

result of this study was to show that process (III) is spectrally unimportant in structures such as (IV), which should provide for it a maximum of opportunity: for a variety of substituents, R, with and without unshared electrons, in the *para*-position in (V), and for purposes of control, in the *meta*-position, and also in the homologous structure (VI),

[1] Baker, Barrett, and Tweed, *J.*, 1952, 2831.
[2] Chierici, Lumbroso, and Passerini, *Bull. Soc. chim.*, 1955, 686.
[3] Mangini and Passerini, *J.*, 1952, 1168; Leandri *et al.*, *Gazzetta*, 1954, **84**, 3, 73; Mangini *et al. ibid.*, p. 47.

did not affect the long-wave band assigned to the chromophore $S{\cdot}C_6H_4{\cdot}NO_2$, except for small modifications attributable to the inductive effect :

$p\text{-}Me_2N{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NO_2\text{-}p$ (IV) $\quad R{\cdot}C_6H_4{\cdot}S{\cdot}C_6H_4{\cdot}NO_2\text{-}p$ (V) $\quad R{\cdot}C_6H_4{\cdot}S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2\text{-}p$ (VI)

Although this was clearly a negative result as regards through-conjugation of the form (III), one could not accept it as excluding the component process (II) in general, because steric twisting in diaryl sulphides might have broken an otherwise effective conjugation. We therefore sought spectral evidence of the octet-enlarging aryl–sulphur conjugation (II) in a more direct way, and, in part, in simpler systems.

The main numerical results (wavelengths and extinction coefficients of band maxima) are in Tables 1—3, and a few of the more significant spectra are illustrated in Figs. 1—3. The following is a summary of the main conclusions.

Starting with methyl phenyl sulphide, benzyl phenyl sulphide, or diphenyl sulphide, a bathochromic shift of a few mμ and intensification of the band near 250 mμ is the general result of introducing the substituents O^- or NH_2 into the *para*-position of the *S*-phenyl group. The red shifts produced by the dimethylamino-group are considerably larger (about 23 mμ) than by the other groups, and therefore the spectral effect of this substituent in other positions, and in other parent compounds, has been studied with some care. It may be noted first that the red shift largely disappears when the dimethylamino-group is introduced into the *meta*-position in methyl phenyl sulphide or diphenyl sulphide, where the formal conjugation between nitrogen and sulphur is removed, and also when the dimethylamino-group is introduced into the *para*-position in methyl phenyl ether and diphenyl ether, where octet expansion is impossible.

These results alone might have suggested that a spectral effect of the conjugative process (II) was under observation in the *p*-dimethylaminophenyl sulphides : but, because of the somewhat small magnitude of the effect, and our inability always to interpret small differences in the spectra of such complex molecules, more extensive control experiments seemed necessary. A series of such controls is included in the record. Two illustrations of their general effect may first be given. These are that a dimethylamino-group, if introduced into the *para*-position of dimethylaniline, or into the *para*-position of the benzyl group of benzyl phenyl sulphide, induces red-shifts of at least half as much as those found in *p*-dimethylaminophenyl sulphides.

In more detail, the following results show how the long-wave band of dimethylaniline, $\lambda_{max.}$ 250 mμ, log ε 4·15, is affected by a series of sulphur-containing *para*-substituents. The figures represent the bathochromic shift Δλ in mμ, and (in parentheses) the intensity log ε of the shifted band :

$S{\cdot}CH_3$	$S{\cdot}C_6H_5$	$S{\cdot}C_6H_4{\cdot}NO_2\text{-}p$	$S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2\text{-}p$
+22 (4·31)	+24 (4·39)	+25 (4·41)	+22 (4·48)
$CH_2{\cdot}S{\cdot}CH_3$	$CH_2{\cdot}S{\cdot}C_6H_5$	$CH_2{\cdot}S{\cdot}C_6H_4{\cdot}NO_2\text{-}p$	
+12 (4·27)	+14 (4·39)	+16 (4·24)	

We see that the excess of the shift when nitrogen–sulphur conjugation of type (II) is formally permitted, over the shift obtaining when it is excluded, is only of the order of magnitude of the latter shift and is therefore not large enough to allow us to conclude that aryl–sulphur conjugation involving octet expansion produces the spectral consequences which have been observed.

Moreover, the original bands at 255 mμ in *p*-aminodiphenyl sulphide and 274 mμ in *p*-dimethylaminodiphenyl sulphide are only very little enhanced by *para*-substitution with NX_2, OR, and O^- (see Table 3).

These results confirm our former provisional conclusion.[4] Sanesi and Leandri recently found no evidence of conjugation of type II in their dipole-moment measurements on aromatic sulphides.[5] It would appear therefore that this form of sulphur conjugation is unimportant in aryl sulphides.

[4] Mangini and Passerini, *loc. cit.*, ref. 3; *J. Phys. Radium*, 1954, **15**, 625; *Gazzetta*, 1954, **84**, 606; *Experientia*, 1956, **12**, 49.

[5] Sanesi and Leandri, *Boll. Sci. Fac. chim. ind. (Bologna)*, 1955, **13**, 56; *Ann. Chim. appl.*, 1955, **45**, 1106.

TABLE 1. *Amino- and hydroxy-substituted sulphides.*

Substituent	Thioanisoles			Benzyl phenyl sulphides *			Diphenyl sulphides		
	No.	λ (mμ)	log ε	No.	λ (mμ)	log ε	No.	λ (mμ)	log ε
H	(1) B. p. 82°/16 mm.	(225	3·05)	(2) M. p. 42—43°	(242	3·62)	(3) B. p. 176—177°/10 mm.	(232	3·76)
		254	3·99		255	3·83		251	4·09
		280	3·00 (*a*)					(265	3·70)
								277	3·76
p-NH_2	(4) B. p. 140°/15 mm.	(220	3·54)	(5) M. p. 74—75°	(227	3·86)	(6) M. p. 96°	(224	3·79)
		242	3·90 (*b*)		248	4·09		240	4·07 (*e*)
		(246	3·97)		255	4·25 (*b*)		255	4·27
		264	4·03		290	3·45 (*d*)		275	3·96 (*d*)
		296	3·14 (*c*)						
p-O^-	(7) M. p. 84—85°	(224	3·64)		not ex.		(8) M. p. 50·1°	(228	3·92)
		259	4·17					260	4·29
		295	3·35 (*d*)						
p-NMe_2	(9) B. p. 140°/3 mm.	(230	3·63)		not ex.		(10) M. p. 66—67°	(228	3·78)
		250	3·93 (*e*)					274	4·39 (*f*)
		272	4·31						
		305	3·39 (*d*)						
m-NMe_2	(11) B. p. 165—166°/16 mm.	238	4·28 (*b*)		not ex.		(12) B. p. 180°/5 mm.	(228	4·03)
		248	4·25 (*d*)					254	4·31 (*g*)
		270	3·63 (*a*)					285	3·68 (*e*)
		(281	2·99)					311	3·53
		308	3·45						

* Substituents in benzyl nucleus.

(*a*) Weak inflexion. (*b*) Ill-defined max. (*c*) Inflexion followed by ill-defined max. (*d*) Inflexion. (*e*) Slight shoulder. (*f*) Max. preceded by very weak shoulder at 250 and 263 mμ. (*g*) Broad band.

(1) *Ber.*, 1887, **20**, 2026: spectrum in *n*-hexane: Mangini *et al.*, *Gazzetta*, 1954, **84**, 3; in EtOH, *idem*, *ibid.*; Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84. (2) *Ber.*, 1907, **40**, 4194: spectrum in EtOH, Fehnel and Carmack, *loc. cit.* (3) Prepared and purified by method (*c*) referred to by Mangini *et al.*, ref. (1): spectrum in EtOH, Fehnel and Carmack, *loc. cit.*; in *n*-hexane: Mangini *et al.*, *loc. cit.*; in ethanol, *idem*, *ibid.*, and *J.*, 1952, 1168; Fehnel and Carmack, *loc. cit.*; Koch, *J.*, 1949, 387; see also, Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5250. (4) *Annalen*, 1912, **393**, 232: spectrum registered in *n*-hexane; in EtOH, Fehnel and Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 2889; in *cyclo*hexane, Tundo and Ruzzier, *Boll. sci. Fac. chim. ind. (Bologna)*, 1956, **14**, 9. (5) *J. Amer. Chem. Soc.*, 1923, **45**, 2399. (6) *Rec. Trav. chim.*, 1912, **31**, 30; spectrum registered in *n*-hexane; in EtOH (envelope $\lambda_{max.}$ 256, log ε 4·28), Mangini *et al.*, *Gazzetta*, 1954, **84**, 47; in *cyclo*hexane, Tundo and Ruzzier, *loc. cit.* (7) *Ber.*, 1914, **47**, 1100; spectrum in 0·1N-NaOH; in EtOH–NaOEt, Fehnel and Carmack, *loc. cit.*, ref. 4. (8) *J. Amer. Chem. Soc.*, 1929, **51**, 1530: spectrum in 0·1N-NaOH; spectral results of Tundo and Ruzzier, *loc. cit.* (9) *Ber.*, 1909, **42**, 3374; spectral results of Tundo and Ruzzier, *loc. cit.* (10) Sanesi and Leandri, *Boll. sci. Fac. chim. ind.* (*Bologna*), 1955, **13**, 56; *Ann. chimica*, 1955, **45**, 1106: spectrum registered in *n*-hexane; in EtOH, Mangini *et al.*, *J.*, 1952, 1168 and *loc. cit.* in (6). (11), (12) See Experimental.

TABLE 2. p-*Substituted dimethylanilines.*

No.	$NMe_2 \cdot C_6H_4X(p)$	λ (mμ)	log ε
(13)	X = H	(>225)	—
	(B. p. 192—193°)	250	4·15
		(274	3·80)
		295	3·35
(16)	X = O⁻	(~230)	—
		245	4·06
		(282	2·94)
		309	3·27
(19)	X = CH_2Ph	(227	3·58)
	(M. p. 31°)	259	4·23
		(283	3·07)
		303	3·32
(22)	X = NMe_2	(228	3·67)
	(M. p. 51°)	264	4·21
		(304	3·27)
		327	3·39
(25)	X = $S \cdot C_6H_4 \cdot NO_2(p)$	(236	3·88)
	(M. p. 180—181°)	252	4·00 (*a*)
		275	4·41
		324	4·15
(14)	X = OMe	(222	3·62)
	(M. p. 48°)	250	4·13
		(285	3·20)
		314	3·41
(17)	X = NH_2	(225	3·60)
	(M. p. 41°)	256	4·08
		(297	3·10)
		323	3·35
(20)	X = $CH_2 \cdot OPh$	(234	3·68)
	(M. p. 119—120°)	261	4·36
		(284	3·21 (*b*)
		301	3·39
(23)	X = $CH_2 \cdot SMe$	(230	3·59)
	(B. p. 123°/5 mm.)	262	4·27
		(286	3·25)
		300	3·38
(26)	X = $CH_2 \cdot S \cdot C_6H_4 \cdot NO_2(p)$	(240	3·99)
	(M. p. 136—137°)	266	4·24
(15)	X = OH	(222	3·58)
	(M. p. 77—78°)	247	4·04
		(284	2·86)
		316	3·40
(18)	X = OPh	(232	3·81)
	(B. p. 192°/16 mm.)	258	4·25
		(289	3·08)
		311	3·38
(21)	X = $CH_2 \cdot C_6H_4 \cdot NMe_2(p)$	(227	3·88)
	(M. p. 91°)	262	4·52
		(284	3·53)
		301	3·67
(24	X = $CH_2 \cdot SPh$	(232	3·82)
	(M. p. 106—107°)	264	4·39
		295	3·65 (*a*)
(27)	X = $S \cdot CH_2 \cdot C_6H_4 \cdot NO_2(p)$	(232	3·89)
	(M. p. 102—103°)	272	4·48

(*a*) Inflexion. (*b*) Min preceded by weak inflexion at 282 mμ, log ε = 3·63. For the compounds 25—27 we report only our results for <300 mμ region; for the region >300 mμ see *Experientia*, 1956, **12**, 49.

(13) Spectrum in *n*-heptane: results of Klevens and Platt, *J. Amer. Chem. Soc.*, 1949, **71**, 1714. (14), (18), (20), (23), (24,) (26), (27) See Experimental. (15) *Ber.*, 1899, **32**, 3681. (16) Spectrum in N-NaOH. (17) *Ber.*, 1875, **8**, 619. (19) *Ann. Chim.*, 1918, **10**, 243. (21) *Chem. Ztg.*, 1900, **24**, 564. (22) *Ber.*, 1903, **36**, 2979: the spectrum is practically coincident with that recorded by Albrecht and Simpson, *J. Amer. Chem. Soc.*, 1955, **77**, 4454. (25) *Boll. sci. Fac. chim. ind.* (*Bologna*), 1955, **13**, 56; *Ann. Chimica*, 1954, **45**, 1106: spectrum in EtOH, Mangini and Passerini, *J.*, 1952, 1165.

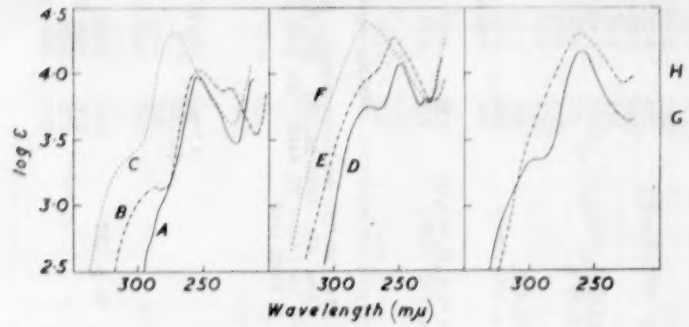
TABLE 3. pp'-*Disubstituted diphenyl sulphides.*

No.		λ (mμ)	log ε
(28)	$p\text{-}NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot NH_2\text{-}p'$	(227	3·85)
	M. p. 108°	250	4·25 (*a*)
		261	4·32
		285	4·02 (*a*)
(29)	$p\text{-}NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot OMe\text{-}p'$	(220	3·95)
	M. p. 94—95°	237	4·11 (*c*)
		258	4·30
		280	3·98 (*a*)
(30)	$p\text{-}NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot OH\text{-}p'$	(220	3·92)
	M. p. 151—152°	233	4·01 (*a*)
		258	4·26
		280	3·93 (*a*)
(31)	$p\text{-}NH_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot O^-\text{-}p'$	(<225)	—
		263	4·35
		282	4·05 (*b*)
(32)	$p\text{-}NMe_2 \cdot C_6H_4 \cdot S \cdot C_6H_4 \cdot NH_2\text{-}p'$	(225	3·72)
	M. p. 130°	250	4·09 (*b*)
		272	4·33
		295	4·00 (*b*)

(*a*) Inflexion. (*b*) Weak inflexion. (*c*) Flat region 235—240 mμ.

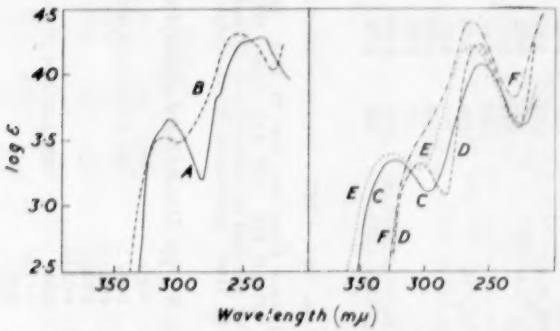
(28) *Ber.*, 1894, **27**, 3262: spectrum in EtOH, Mangini *et al.*, *J.*, 1952, 1168; *Gazzetta*, 1954, **84**, 47. (29) *J. Amer. Chem. Soc.*, 1930, **52**, 1146: spectrum in EtOH, Mangini *et al.*, *Gazzetta*, *loc. cit.* (30) *J. Amer. Chem. Soc.*, 1934, **56**, 1978. (31) Spectrum in N-NaOH. (32) Mangini *et al.*, *loc. cit.*; spectrum registered in *n*-hexane; in EtOH, Mangini *et al.*, *loc. cit.*

FIG. 1.



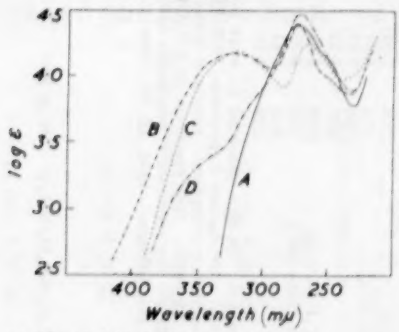
A, Ph·S·CH_3 in hexane.
B, *p*-$H_2N·C_6H_4·S·CH_3$ in hexane.
C, *p*-$(CH_3)_2N·C_6H_4·S·CH_3$ in *cyclo*hexane.
D, Ph·S·Ph in hexane.
E, *p*-$H_2N·C_6H_4·S·Ph$ in hexane.
F, *p*-$(CH_3)_2N·C_6H_4·S·Ph$ in hexane.
G, *p*-$\bar{O}·C_6H_4·S·CH_3$.
H, *p*-$\bar{O}·C_6H_4·S·Ph$.

FIG. 2.



A, *m*-$(CH_3)_2N·C_6H_4·S·CH_3$ in *cyclo*hexane.
B, *m*-$(CH_3)_2N·C_6H_4·S·Ph$ in *cyclo*hexane.
C, *p*-$H_2N·C_6H_4·N(CH_3)_2$ in *cyclo*hexane.
D, *p*-$(CH_3)_2N·C_6H_4·CH_2Ph$ in *cyclo*hexane.
E, *p*-$(CH_3)_2N·C_6H_4·N(CH_3)_2$ in *cyclo*hexane.
F, *p*-$Ph·S·CH_2·C_6H_4·N(CH_3)_2$ in *cyclo*hexane.

FIG. 3.



A, *p*-$(CH_3)_2N·C_6H_4·S·Ph$ in *cyclo*hexane.
B, *p*-$NO_2·C_6H_4·S·C_6H_4·N(CH_3)_2$-*p* in hexane.
C, *p*-$NO_2·C_6H_4·S·CH_2·C_6H_4·N(CH_3)_2$-*p* in *cyclo*hexane.
D, *p*-$NO_2·C_6H_4·CH_2·S·C_6H_4·N(CH_3)_2$-*p* in *cyclo*hexane.

Experimental

Spectra were determined with a Hilger Uvispek photoelectric spectrophotometer. The concentrations used were 10^{-5}M. The compounds were measured in *cyclo*hexane (or in *n*-hexane, as indicated in the Tables) in order to reduce the solvent effect. The results are reported in Tables 1—3, where the wavelengths of maxima and minima are given as mμ, and extinction values as log ε : minima are indicated in parentheses.

References are given in the Tables to the methods used in the preparation of the compounds, and also references to spectra already recorded by other authors and in other solvents. The absorption curves are reproduced in Figs. 1—3.

The following descriptions relate to the preparation of new compounds or of known compounds by modified methods.

m-*Dimethylaminodiphenyl sulphide* was prepared as follows. *m*-Aminodiphenyl sulphide [6] (10 g.) was suspended in water (100 c.c.), and sodium hydrogen carbonate (13 g.) and then dimethyl sulphate (16 g.) were added with constant stirring. The mixture was kept at 30° until evolution of carbon dioxide had ceased, and then at 50—60° for 30—60 min. On cooling, an oil separated (together with a small amount of a crystalline product which was neglected) and was extracted with ether. Distillation of the dried ether extract afforded an oil, b. p. 180—181°/5 mm. (Found : N, 6·1. $C_{14}H_{15}NS$ requires N, 6·1%).

m-Dimethylamino(thioanisole) was obtained in better yield and more easily by methylation of *m*-amino(thioanisole) as above than by distillation of the quaternary iodide. The product had b. p. 165—166°/16 mm. *p*-Methoxydimethylaniline, obtained by methylation of *p*-anisidine as indicated above, crystallised from water in plates, m. p. 48° (in agreement with Griess,[8] who obtained it by distillation of the quaternary iodide). NN-*Dimethyl*-p-*phenoxyaniline* was prepared similarly from *p*-aminodiphenyl ether, as an oil, b. p. 193°/16 mm. (Found : N, 6·7. $C_{14}H_{15}ON$ requires N, 6·6%).

p-*Dimethylaminobenzyl phenyl ether*. A solution of *p*-dimethylaminobenzyl alcohol (5 g.) in concentrated hydrochloric acid (25 c.c.) was heated for 2 hr. in a sealed tube [9] at 100°, and to the cooled reaction mixture, which contained *p*-dimethylaminobenzyl chloride, was added aqueous-ethanolic sodium phenoxide (2·5 g. of phenol in 50 c.c. of ethyl alcohol and 60 c.c. of aqueous 20% NaOH). The mixture was refluxed for 15 min.; after cooling, a white product was separated. Crystallization from ligroin gave the *ether* as needles, m. p. 119—120° (Found : N, 6·2. $C_{15}H_{17}ON$ requires N, 6·2%).

p-*Dimethylaminobenzyl methyl sulphide* was prepared as was the preceding ether, except that the *p*-dimethylaminobenzyl chloride was condensed with sodium thiomethoxide in a sealed tube. Extraction of the solution with ether yielded an oil, which on distillation had b. p. 123°/5 mm. (Found : N, 7·9. $C_{10}H_{15}NS$ requires N, 7·7%). p-*Dimethylaminobenzyl phenyl sulphide* was prepared similarly from *p*-dimethylaminobenzyl chloride and sodium thiophenoxide. It separated in plates, m. p. 106—107°, from ethanol (Found : N, 5·9. $C_{15}H_{17}NS$ requires N, 5·75%). p-*Dimethylaminobenzyl* p-*nitrophenyl sulphide*, prepared from *p*-dimethylaminobenzyl chloride and sodium *p*-nitrothiophenoxide, crystallized from *iso*propyl alcohol in orange-yellow plates, m. p. 136—137° (Found : N, 9·7. $C_{15}H_{16}O_2N_2S$ requires N, 9·7%). p-*Dimethylaminophenyl* p-*nitrobenzyl sulphide* was prepared from a solution of dimethylaminothiophenol (10 g.) in aqueous sodium hydroxide (3 g. in 30 c.c.) and an ethanolic solution (150 c.c.) of *p*-nitrobenzyl bromide (15 g.). After the mixture had been refluxed for 15 min. a red crystalline product separated on cooling, and crystallized from ligroin in prisms, m. p. 102—103° (Found : N, 9·72. $C_{15}H_{16}O_2N_2S$ requires N, 9·79%).

This work has benefited from a financial contribution from the Italian "Consiglio Nazionale Ricerche." The authors are indebted to Prof. C. K. Ingold, F.R.S., for helpful discussion.

Istituto Chimica Industriale,
Università degli Studi, Bologna, Italy.
[Present address (R. P.) : Istituto Chimica Organica Industriale,
Università Studi, Catania, Corso Italia 21, Italy.] [*Received, May 9th*, 1956.]

[6] Hünig, *Chem. Ber.*, 1952, **85**, 1056.
[7] Zincke and Muller, *ibid.*, 1913, **46**, 781.
[8] Griess, *ibid.*, 1880, **13**, 249.
[9] As described by Barun and Kruber, *Ber.*, 1912, **45**, 2992.

963. *Energy Levels and Absorption of Some Monosubstituted Benzene Derivatives.*

By A. Mangini and C. Zauli.

In order to obtain further information on the most important electronic structures which contribute to the molecular state in photochemical excitation, the energy levels of molecules such as Ph·X·R (X = O, S; R = Me) have been calculated by the valence-bond (V.B.) method.

The present theoretical results are perfectly consistent with the previous empirical assignment of the bands in thioanisole and diphenyl sulphide: absorption in the 250 mμ region is essentially due to a modified transition of the B_{2u} type, while that in the 275—280 mμ region arises from a transition due to the conjugative interaction of the $3p\pi$ electrons of sulphur with the phenyl ring ($\overbrace{C_6H_5\text{–}\ddot{S}\text{–}}^{\bullet}$ chromophore).

The second phenyl group in diphenyl sulphide is practically ineffective in changing the absorption.

In the analogous oxygenated compounds, anisole and diphenyl ether, the conjugative interaction of *O*-phenyl is significantly weaker than that of *S*-phenyl: the absorption bands in the 220 and the 260—280 mμ region being of B_{1u} and B_{2u} type. Our calculations confirm that in the photo-excited state the mesomeric effect of sulphur is greater than that of oxygen.

The absorption curves of thioanisole, diphenyl sulphide, anisole, and diphenyl ether in *n*-hexane solution (in ethanol there are negligible modifications) are characterized, in the near ultraviolet region, by two bands as shown below (λ max. in mμ, i = inflection point, f.s. = fine structure; the type of each band is also indicated):

	λ max.	log ε	λ max.	log ε
Thioanisole	254 (B_{2u})	3·99	280 (π_n^* chromophore)	~ 3·00 (i)
Diphenyl sulphide	251 (B_{2u})	4·09	277 (π_n^* chromophore)	3·76
Anisole	219 (E_{2u},* B_{1u})	3·90	265—278 (B_{2u})	~3·20 (f.s.)
Diphenyl ether	219 (E_{2u},* B_{1u})	4·00	265—278 (B_{2u})	~3·20

* Dunn and Ingold, *Nature*, 1955, **176**, 65.

Mangini and Passerini,[1] investigating the spectroscopic modifications in the near ultraviolet region shown by some alkyl phenyl and diphenyl sulphides, suggested on empirical grounds that such bands arise essentially from the excitation of the six electrons in a benzenoid chromophore, $\overbrace{\text{Ph}\cdot}$, conventionally labelled π^6 (obviously modified by ·SMe or ·SPh acting as side-chain), and from the eight electrons in a chromophore $\text{Ph}\cdot\ddot{\underset{(\cdot\cdot)}{S}}$, arising from interaction of the unshared pair of $3p$ sulphur electrons with the π-shell of the phenyl ring. Such a classification differs from both that of Platt[2] and that of Robertson and Matsen:[3] in the analogous oxygenated systems, anisole and diphenyl ether, the situation is substantially different, and in the longer-wavelength absorption region the sequence of transitions is reversed. This could indicate that in the photoexcited state the mesomeric effect of sulphur is larger than that of oxygen, contrary to what occurs in the ground state[4] or transition state.[5] In previous work, Mangini and Passerini attempted to interpret—although qualitatively—the phenomenon.[6]

The purpose of the present investigation is to study the electronic state of the molecules

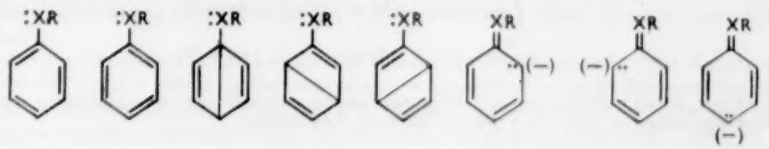
[1] Mangini and Passerini, *J.*, 1952, 1168.
[2] Platt, *J. Chem. Phys.*, 1951, **19**, 101.
[3] Robertson and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5243, 5248, 5250.
[4] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953.
[5] Baker, Barrett, and Tweed, *J.*, 1952, 2831.
[6] Mangini and Passerini, *Gazzetta*, 1954, **84**, 606.

Ph·X·R (I), where X = O or S; R = alkyl or phenyl, in order to acquire further information, less empirical, on the most important valence-bond structures which take part in the molecular state during the photochemical excitation.

The valence-bond method has been followed, avoiding semi-empirical parameters, but where possible developing the necessary formulæ rigorously.

Molecules Ph·X·R (R = alkyl).—We can assume that, in this case, the influence of R on the electronic states is of lower order, or at least has an almost constant weight on the first few energy levels: this simplifies the problem to discussion of a molecule of type $C_6H_5-\ddot{X}-$ having C_{2v} symmetry. For such molecules we have considered resonance as occurring between the 8 limiting structures (II). If we call Γ_i the reducible representation of the C_{2v} group coming from the above 8 structures, it can be shown that $\Gamma_i = 5A_1 + 3B_1$.

(II)



K_1 K_2 D_1 D_2 D_3 P_1 P_2 P_3

Wave functions of types A_1 and B_1, respectively, will be of the forms:

$$\Psi_{A_1} = c_1(K_1 + K_2) + c_2D_1 + c_3(D_2 + D_3) + c_4(P_1 + P_2) + c_5P_3 \quad . \quad (1)$$

$$\Psi_{B_1} = d_1(K_1 - K_2) + d_3(D_2 - D_3) + d_2(P_1 - P_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the c's and d's are certain coefficients.

From our previous calculations of the energies concerned with structures P_3 and $(D_2 - D_3)$ these can be left aside in the mesomeric system (II) because their energy is too high to exert any effective influence in the first excited levels; analogously, it can be shown that structures D_1 and $(D_2 + D_3)$ differ only very slightly. Functions (1) and (2) can now be written

$$\Psi_{A_1} = c_1(K_1 + K_2) + c_2(D_1 + D_2 + D_3) + c_4(P_1 + P_2) \quad . \quad . \quad (3)$$

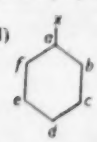
$$\Psi_{B_1} = d_1(K_1 - K_2) + d_2(P_1 - P_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Each structure in equations (3) and (4) has been expressed by a combination of determinantal basic functions (1), with eigenvalues $S_s = 0$: [7]

$$\begin{Bmatrix} a\ b\ c\ d\ e\ f\ x\ y \\ \alpha\ \beta\ .\ .\ .\ .\ \beta\ \alpha \end{Bmatrix}$$

where a, b, c, d, e, f represent the atomic eigenfunctions of carbon atoms in the benzene ring (III), x that of the hetero-atom, $y = x$, b, or f, depending on the particular structure considered, and α and β are the spin-functions. Substituting such linear combinations in the matrix elements of the secular equations derived from (3) and (4) and making use of symmetry, one can obtain all H_{ij} and S_{ij}; these can be written as sums of integrals between the basic functions.

(III)



According to the rigorous valence-bond method, the latter have to be developed as a function of the exchange intergrals of all orders. Such an operation is practically impossible for the extremely high number of exchange integrals which occur between two basic functions with eight electrons. The development of the calculation has been accomplished up to triple exchanges inclusive as shown in the Table.

As the values of integrals between two basic functions are independent of the symmetry operations, we have taken advantage of the fact that the basic functions of the problem can be derived from those of benzene by a product of $x(\beta)x(\alpha)$. Now the perturbation due to these orbitals may be considered nearly equal in the integrals between two basic functions

[7] Eyring, Walter, and Kimball, "Quantum Chemistry," J. Wiley, New York, 1944.

TABLE.

We set

$$\int ab \ldots\ldots M\, ba \ldots\ldots d\tau = A^2$$

$$\int ac \ldots\ldots M\, ca \ldots\ldots d\tau = B^2$$

$$\int ad \ldots\ldots M\, da \ldots\ldots d\tau = C^2$$

$$\int ax \ldots\ldots M\, xa \ldots\ldots d\tau = S^2_1$$

$$\int bx \ldots\ldots M\, xb \ldots\ldots d\tau = S^2_2$$

$$\int cx \ldots\ldots M\, xc \ldots\ldots d\tau = S^2_3$$

$$\int dx \ldots\ldots M\, xd \ldots\ldots d\tau = S^2_4$$

with $M = 1$, H and writing down only the atomic functions which do not correspond in the two members of exchange integrals. With this position we have, for example,

$$\int abcdefxx\ M\ bdcaexfx\ d\tau = ABCS_3$$

Symmetry A_1:

$$H_{11} = 4\Big\{5Q + 12A^2 - 24B^2 - 3C^2 - 5S_1^2 - 10S_2^2 - 10S_3^2 - 5S_4^2 + 14B^2 - 30A^2B - 24ABC + 20BS_1S_3 + 10BS_2^2 + 20BS_3S_4 + 10BS_3^2 - 12AS_1S_3 - 12AS_2S_3 - 12AS_3S_4\Big\}$$

$$H_{22} = 4\Big\{9Q + 18A^2 - 54B^2 + 9C^2 - 9S_1^2 - 18S_2^2 - 18S_3^2 - 9S_4^2 + 36B^2 - 36A^2B - 72ABC + 36BS_1S_3 + 20BS_2^2 + 36BS_3S_4 + 20BS_3^2 - 16AS_1S_3 - 16AS_2S_3 - 16AS_3S_4 - 16CS_2S_3 - 8CS_1S_4\Big\}$$

* $H_{33} = 4\Big\{4Q + 4A^2 - 8\overline{A}^2 - 8B^2 - 8\overline{B}^2 - 4C^2 - 4\overline{C}^2 - 4S_1^2 - 2S_2^2 - 4\overline{S}_2^2 - 4S_3^2 - 2S_4^2 + 6B^2 - 12A^2B + 6ABC - 12AS_1S_3 - 2AS_2S_4 + 4BS_2^2 + 2BS_3^2 - 8BS_1S_3 + 6BS_2S_4 - 4CS_1S_4 + 6CS_2S_3 + 2\overline{B} - \overline{A}^2 + 2\overline{B}^2 - 8\overline{A}\overline{C} - \overline{S}_2^2 - 16B^2 + 10A^2B + 6ABC + 5BC^2 - 2AS_1S_3 + 3AS_2S_4 + 2BS_1^2 - 2BS_2^2 - 2BS_3^2 - BS_4^2 - BS_2S_3 - 2BS_2S_4 + 30S_2S_3\Big\}$

$$H_{12} = -4\Big\{6Q + 18A^2 - 36B^2 - 6S_1^2 - 12S_2^2 - 12S_3^2 - 6S_4^2 + 24B^2 - 36A^2B - 36ABC + 28BS_1S_3 + 14BS_2^2 + 28BS_2S_4 + 14BS_3^2 - 16AS_1S_3 - 16AS_2S_3 - 16AS_3S_4 - 4CS_2S_3 - 4CS_1S_4\Big\}$$

$$H_{13} = 4\Big\{5S_2 - 4CS_3 - 4AS_3 - 10AS_1 - BS_4 + 10ABS_1 + 12ABS_3 + 10BCS_1 + 4BCS_3 - 21BS_2S_3 - 4C^2S_2 + 15A^2S_2 - B^2S_2 + 7ACS_4 - ACS_2 - 7S_2^3 - 3S_2S_4^2 + 3S_1S_4^2 - 2S_2S_3^2 - S_2S_4^2\Big\}$$

$$H_{23} = -4\Big\{6S_2 - 6CS_3 - 6AS_3 - 12AS_1 + 12ABS_1 + 18ABS_3 + 12BCS_1 + 4BCS_3 - 31B^2S_2 - C^2S_2 + 16A^2S_2 - 2B^2S_4 + 6ACS_4 - 9S_2^3 - 4S_2S_4^2 + 3S_1S_2^2 - 2S_2S_4^2\Big\}$$

Symmetry B_1:

$$H_{11} = 4\Big\{3Q - 9C^2 - 3S_1^2 - 6S_2^2 - 3S_4^2 - 6S_3^2 - 6B^2 - 18A^2B + 12CS_2S_3 - 8CS_1S_4\Big\}$$

$$H_{22} = 4\Big\{4Q + 4A^2 - 8\overline{A}^2 - 8B^2 - 8\overline{B}^2 - 4C^2 - 4\overline{C}^2 + 4S_1^2 - 2S_2^2 - 4S_3^2 - 2S_4^2 + 6B^2 - 12A^2B + 6ABC - 4S_3^2 - 12AS_1S_3 - 2AS_2S_4 + 4BS_2^2 + 2BS_3^2 - 8BS_1S_3 + 6BS_2S_4 - 4CS_1S_4 - 6CS_2S_3 - 2\overline{B} - \overline{A}^2 + 2\overline{B}^2 - 8\overline{A}\overline{C} - \overline{S}_2^2 - 16B^2 + 10A^2B + 6ABC + 5BC^2 - 2AS_1S_3 + 3AS_2S_4 + 2BS_1^2 - 2BS_2^2 - 2BS_3^2 - BS_4^2 + BS_2S_3 - 2BS_2S_4 + 3CS_2S_3\Big\}$$

$$H_{12} = 4\Big\{3S_2 - 6AS_1 - 3BS_3 - 3BS_4 - 6ABS_1 + 4BCS_1 - B^2S_2 - 8C^2S_2 + 3A^2S_2 + 3B^2S_4 + 2ABS_3 + 3ACS_4 + 3ACS_3 - 3S_2^3 + S_2S_4^2 + 3S_1S_2^2 - 6S_2S_3^2 - S_2S_4^2\Big\}$$

* The integrals so marked refer to the polar atom.

having the same spin distribution in the benzenic orbitals or reducible to this by symmetry operations.* This is approximately true only if the integral between two basic functions does not involve a coulombic integral.

The values of the exchange integrals have been considered independently of the atomic functions which do not participate in the exchange,† except for double exchange integrals in polar structures.

The numerical calculation should now be possible. At first we used the values for Z proposed by Zener and Slater,[8] but as these values do not lead to good results,[8a] we have used those proposed by Kohlrausch :[9] unfortunately, with the latter values the matrix elements converge slowly as we increase the order of exchange integrals added. Even exchange integrals of higher order than triple still have noticeable values, and it is necessary to introduce them in the expression for the matrix elements. This, of course, complicates the problem.

We have therefore tried to find a method which could allow the introduction of exchanges of higher order without requiring the complete development of integrals between two basic functions. We have obtained S_{ij} elements as follows : in the integral between two basic functions one can exchange only atomic eigenfunctions having the same spin : now, all the exchanges between atomic eigenfunctions with spin α and then with spin β having been made, all the other exchanges result from their combination. Such a situation is expressed by the following formula : ‡

$$S = (-1)^{R_0} S_{0\alpha} S_{0\beta} + S_{0\beta} \sum_n (-1)^{p_n + R_0} S_{\alpha n} + S_{\alpha 0} \sum_n (-1)^{q_n + R_0} S_{\beta n} + \\ + \sum_n (-1)^{p_n} S_{\alpha n} \sum_n (-1)^{q_n} S_{\beta n}$$

where $S_{0\alpha}$ and $S_{0\beta}$ are the overlap values of exchange between the atomic eigen-functions with spin α and β respectively of the first exchange integral; R_0 is the number of exchanges necessary to have the starting function from the first exchange integral; $S_{\alpha n}$ and $S_{\beta n}$ are the values corresponding to the overlap of the n-th exchange between atomic eigen-function of α-spin and β-spin among themselves; p_n and q_n are the number of exchanges necessary to obtain distribution α or β respectively from the n-th exchange in the first exchange integral.

When calculating the values of the matrix elements H_{ij}, the method followed by us takes advantage of the regularity shown by H_{ij} with subsequent additions of double, triple, . . . exchange integrals. If one compares the successive values with the corresponding overlap integrals, it is possible to make quite a good extrapolation to the final value with all orders of exchange.

By following this method it is possible to calculate the secular equations for the problem of the electronic states in any molecule of the type Ph·Ẍ·Alk.

Molecules Ph·Ẍ·Ph.—The problem is now more complicated because of the larger number of π electrons. It is obvious that we must introduce additional approximations : first we shall consider the molecule Ph·Ẍ·Ph as composed of two parts : Ph·Ẍ· and ·Ph.

This assumption implies the disappearance of symmetry in the molecule during our calculations. Certain other effects also have to be regarded as less important, for example :

(i) The splitting of levels due to symmetry (interaction of the two structures $\overbrace{(1)\ C_6H_5\text{–}\ddot{X}\text{–}C_6H_5\ (2)}$ and $\overbrace{(2)\ C_6H_5\text{–}\ddot{X}\text{–}C_6H_5\ (1)}$; this interaction is probably not very

* This is justified by the fact that overlap of the atomic function of the hetero-atom with the atomic function of the carbon atoms of the benzene nucleus decreases rapidly with the increase in distance : the exchange integrals of high order involving the atomic eigenfunction of the hetero-atom, therefore, lead to very little difference.

† This is demonstrable if the atomic integrals having many centres are calculated with Mulliken approximations.

‡ It is noteworthy that analogous formulæ can be derived for the H_{ij} : this way of working—although more rigorous—is very difficult, and the method to be described later has been preferred.

[8] Zener, *Phys. Rev.*, 1930, **36**, 51; Slater, *ibid.*, p. 57.

[8a] See also Scrocco and Salvetti, *Ricerca sci.*, 1953, **23**, 1410.

[9] Kohlrausch, *Acta Phys. Austriaca*, 1950, **3**, 452.

important, since the absorption spectra of compounds Ph·Ẍ·Ph are very similar to those corresponding to the alkyl-aryl type.

(ii) The interaction of $p\pi$ electrons of the heteroatom X with the $2p\pi$ electrons of the second benzene ring (we have, however, taken some account of this interaction by introducing in the values of the matrix elements in connection with the part Ph·, half of the calculated value of the perturbation of the $p\pi$ electrons of X already found when solving the problem of the structure Ph·Ẍ·).

(iii) The interaction benzene nucleus(1)–benzene nucleus(2) (this can almost certainly be considered very unimportant as it should play almost an identical rôle in the first few energy levels whatever the central atom X).

This procedure, although not absolutely orthodox, could represent a good approximation to the real state of the molecule. It is also known that molecules of the type considered are not coplanar.

We must therefore take into consideration not only the different interaction of the $2p\pi$-orbitals of the benzene nucleus with the $p\pi$-orbitals of the X atom, but also the interaction between the latter and the σ skeleton of the molecule. In practice only the exchange integrals between the p-orbitals of the hetero-atom and the two trigonal orbitals σ_1 and σ_2 of the nearby carbon atom will be of importance, together with the trigonal orbitals of atoms b and f, σ_3 and σ_4, which form a σ-bond with the former.

A priori this σ–π interaction would not appear to be negligible because at first it seems to be different for covalent and polar structures (in the latter there is only one p-atomic orbital on the herero-atom). There are, on the other hand, strong reasons to believe that such interaction should have a constant weight in the first two excited levels with which we are concerned.

These considerations are based on the following points: (iv) The angle which the X orbitals form with the plane of the ring varies over the range 50—60°; this fact, together with the consideration that the σ-orbitals are sp^2 hybrids, makes the overlap integral and the exchange integral between the σ and X orbitals have not very large values.

(v) The interaction energy σ–π which we call $E_{\sigma\pi}$ is formed by an addition of exchange integrals of various orders. Owing to the spatial position of the $3p_z$ orbital of sulphur one can *a priori* affirm that the terms having the most weight in this addition are the double exchange integrals (with a *minus* sign for " repulsion ") and only those derived from the latter for the successive exchange between two atomic eigenfunctions: *e.g.*, the triple and quadruple, having a *plus* sign. These to some extent compensate for the value of the double integrals. Such compensation could be approximately considered as 1/3 (maybe more than less); because if we have a certain distribution of orbitals, increasing the order of exchange integrals, the number of distinct ways in which they could be built up is also increased. Although it is not possible to give a quantitative value to $E_{\sigma\pi}$, it is clear that for all these reasons one should expect a very small value when compared with that one of the energy corresponding to structures considered in the problem of the molecule Ph·Ẍ·.

(vi) The values of energy for the structures which we have considered in our problem are obtained from equation (5).

$$E_L = \frac{\int \Psi_L H \Psi_L d\tau}{\int \Psi_L \Psi_L d\tau} \qquad \ldots\ldots\ldots \quad (5)$$

If we neglect the contribution of the term $S_{\sigma\pi}$ which represents the overlap of σ–π we can write

$$E_L = E_{L\pi} + \frac{\sum_{\sigma\pi} (\text{Exchange integral})}{S_\pi} \qquad \ldots\ldots \quad (6)$$

where $E_{L\pi}$ is the π-energy of the L structure, S_π the corresponding overlap, and $\sum_{\sigma\pi}$ (Exchange integral) is the sum of the exchange integrals between the $3p_z$ orbital of sulphur and the trigonal orbitals of carbon aroms. Now, in the polar structures the term

S_π is about one-half of the corresponding term for the covalent structures; the sum $\sum_{\sigma-\pi}$ (Exchange integral) for the covalent structures is about twice that for the polar structures.

The value $E_{\sigma-\pi}$ is now a constant for the covalent and polar structures. Also the interaction between the two types of structures has approximately the same value.

For this reason we can consider the difference of energy between two levels as independent of the interaction σ–π. In no case is the assignment of transitions affected. The problem is therefore related both to the previous one and to that of finding the matrix elements when the perturbation of the electrons of the hetero-atom have been added to the original phenyl.

When dealing with the lower energies of Ph•, which are principally due to structures of covalent type, we have followed the same procedure as indicated in the previous paragraph, and expressed the matrix elements as functions of integrals between two basic functions; these, which result from six atomic eigenfunctions, are easily written as functions of exchange integrals of all orders, without its being necessary to use any approximation such as the interpolation scheme previously described.

Calculation and Results.—We proceeded as just indicated in the case of anisole (I; X = O), thioanisole (I; X = S), and diphenyl sulphide (I; R = Ph, X = S) with particular consideration to the last; we have also taken into account the fact that the planes in which the two benzene rings lie form an angle of 72°. The atomic eigenfunctions are those of Slater's type without nodes. The exchange integrals have been expressed as a function of integrals between atomic eigenfunctions, following the usual method.

The calculations have been accomplished, when possible, by following the interpolation formulæ of Scrocco and Salvetti [10] or of other authors,[11,12] the following parameters being used: distance C–C 2·63 a.u., distance C–O 2·59 a.u., and Z values, $Z_O = 2{\cdot}088$,* $Z_O = 2{\cdot}90$.[9]

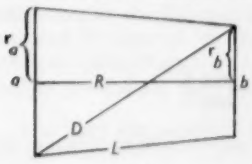
The integrals where the 3p sulphur electrons were involved have been calculated as follows: Kohlrausch's paper [9] indicates the procedure to obtain the orbital radii from the screening constants. If we express these values in atomic units, the values of atomic repulsions are

$$(aa/bb) = 1/L + 1/D \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

obtained * from (7), where L and D are as indicated in (IV) and R is the internuclear distance between the atoms a and b. This is equivalent to considering the electronic cloud as " concentrated " in two half-charges set over the extremities of the radii of the orbitals.

The distance carbon–sulphur has been taken equal to 3·33 a.u., and the charge $Z_S = 2{\cdot}64$.[9]

The calculation of integrals of type $(xx\overset{+}{V}y)$ has been made by Sklar's method,[13] and the values of $\overline{Z}$ necessary for the calculation are: $\overline{Z}_O = 3{\cdot}66$, $\overline{Z}_O = 4{\cdot}94$, $\overline{Z}_S = 4{\cdot}08$. For integrals with more than two centres we adopted Mulliken's approximation. For the electroaffinity of carbon we used the value 0·069 Å proposed by the same author.[14] The ionization potentials are the following: $I_O = 11{\cdot}27$ e.v.,[15] I_O† $= 12{\cdot}6$ e.v., $I_S = 10{\cdot}36$ e.v.[15]



(IV)

On the basis of values obtained by the above method, we calculated all necessary exchange integrals. Also we grouped together the invariable terms such as nuclear repulsion and ionization potentials, so that every integral could be expressed in the form $SQ - A$, S being the overlap of such an integral, Q the coulombic term from which arises the particular exchange integral, and A is expressed in atomic units.

* A better formula is $(aa/bb) = (1 - S_{ab}^4)/L + 1/D$, where $S_{ab} = \int \phi_a \phi_b \, d\tau$.

† We have used the value which oxygen has in the water molecule following Price and Sugden (*Trans. Faraday Soc.*, 1948, **44**, 116).

[10] Scrocco and Salvetti, *Ricerca sci.*, 1952, **22**, 1766.
[11] Barnett and Coulson, *Phil. Trans.*, 1951, **243**, 221.
[12] Roothaan, *J. Chem. Phys.*, 1951, **19**, 1445.
[13] Sklar and Liddane, *ibid.*, 1939, **7**, 374.
[14] Mulliken, *ibid.*, 1934, **2**, 782.
[15] Landolt-Börnstein, " Zahlenwerte und Functionen," I Band, I Teil, 1950.

By substituting the values obtained for the exchange integrals in the expression for the matrix elements and interpolating for the higher-order exchanges as already indicated, it has been possible to write the secular equations for thioanisole and anisole.

Putting $X = Q - E$, where Q is the coulombic integral and E the energy, we obtained the secular equations:

Thioanisole

$$A_1 \left| \begin{array}{ccc} (x + 0{\cdot}054) & -0{\cdot}9824(x + 0{\cdot}040) & 0{\cdot}1256(x - 1) \\ -0{\cdot}9824(x + 0{\cdot}040) & (x + 0{\cdot}065) & -0{\cdot}1343(x - 1) \\ 0{\cdot}1256(x - 1) & -0{\cdot}1343(x - 1) & (x + 0{\cdot}210) \end{array} \right| = 0$$

$$B_1 \left| \begin{array}{cc} (x + 0{\cdot}336) & -0{\cdot}051(x + 1) \\ -0{\cdot}051(x + 1) & (x + 0{\cdot}456) \end{array} \right| = 0$$

Anisole

$$A_1 \left| \begin{array}{ccc} (x + 0{\cdot}126) & -0{\cdot}9830(x + 0{\cdot}123) & 0{\cdot}2083(x - 1) \\ -0{\cdot}9830(x + 0{\cdot}123) & (x + 0{\cdot}131) & -0{\cdot}2176(x - 1) \\ 0{\cdot}2083(x - 1) & -0{\cdot}2176(x - 1) & (x + 0{\cdot}312) \end{array} \right| = 0$$

$$B_1 \left| \begin{array}{cc} (x + 0{\cdot}365) & 0{\cdot}0123(x - 1) \\ 0{\cdot}0123(x - 1) & (x + 0{\cdot}520) \end{array} \right| = 0$$

Therefore the lower excitation energies have the following values:

	Calc.	Found
Thioanisole:		
I excited (A_1)	4·55 e.v. ~2730 Å	2750 Å.
II „ (B_1)	4·73 e.v. ~2630 Å	2540 Å
Anisole:		
I excited (B_1)	4·85 e.v. ~2560 Å	2600—2800 Å
II „ (A_1)	5·80 e.v. ~2140 Å	2200 Å

There is therefore good agreement between the calculated and experimental values.

Passing to diphenyl sulphide, we have also to consider in our calculation steric hindrance, bearing in mind the fact that exchange integrals are approximately proportional to the corresponding overlap integrals. The secular equations for the Ph·S̈· group are:

$$A_1 \left| \begin{array}{ccc} (x - 0{\cdot}0114) & -0{\cdot}9818(x - 0{\cdot}0242) & 0{\cdot}0992(x - 1) \\ -0{\cdot}9818(x - 0{\cdot}0242) & x & -0{\cdot}1125(x - 1) \\ 0{\cdot}0992(x - 1) & -0{\cdot}1125(x - 1) & (x + 0{\cdot}253) \end{array} \right| = 0$$

$$B_1 \left| \begin{array}{cc} (x + 0{\cdot}3712) & -0{\cdot}0370(x + 2) \\ -0{\cdot}037(x + 2) & (x + 0{\cdot}363) \end{array} \right| = 0$$

Solving these, we have the following solutions:

$$\begin{array}{ll} A_1 & E_0 = Q - 0{\cdot}049 \\ A_1 & E_1 = Q + 0{\cdot}298 \\ B_1 & E_2 = Q + 0{\cdot}314 \end{array}$$

which correspond to the following excitation energies

I excited (A_1)	4·72 e.v., 2640 Å
II „ (B_1)	4·95 e.v., 2500 Å

The weights of the various structures in the various states may be shown to be approximately as follows:

A_1: fundamental	$0{\cdot}48(K_1 + K_2)$	$0{\cdot}40(D_1 + D_2 + D_3)$	$0{\cdot}12(P_1 + P_2)$
I excited	$0{\cdot}15(K_1 + K_2)$	$0{\cdot}85(P_1 + P_2)$	
B_1: II „	$0{\cdot}55(K_1 - K_2)$	$0{\cdot}45(P_1 - P_2)$	

For the phenyl group, operating as already described, we have the following secular equations:

$$A_{1g} \left| \begin{array}{cc} (x - 0{\cdot}0721) & -0{\cdot}9829(x - 0{\cdot}0844) \\ -0{\cdot}9829(x - 0{\cdot}0844) & (x - 0{\cdot}0594) \end{array} \right| = 0$$

$$B_{2u} \left| \begin{array}{c} x + 0{\cdot}2885 \end{array} \right| = 0$$

These give, for the fundamental and the first excited states, the following energies: $\overline{E}_0 = Q - 0{\cdot}0761$, $\overline{E}_1 = Q - 0{\cdot}2885$, corresponding to an excitation energy of 4·95 e.v. (2500 Å).

The weights of the structures in the two levels considered are as follows :

A_{1g}	0·67 $(K_1 + K_2)$	0·33 $(D_1 + D_2 + D_3)$
B_{2u}	$(K_1 - K_2)$	

Following the approximations, discussed on p. 4963, the molecular functions for diphenyl sulphide come from the product of the molecular functions of groups Ph·$\ddot{X}$· and C_6H_5·; the energy levels result from the addition of the energy levels of the two parts.

Let us call the sum of the coulombic integrals relative to the two partial problems W. Then the first four energy levels, to which correspond the first three transitions, are the following (where $\overline{E}_0$ and $\overline{E}_1$ are the energies relative to phenyl; E_0, E_1, E_2, those relative to Ph·S·) :

$$E_0 + \overline{E}_0 = W - 0{\cdot}125 \qquad E_2 + \overline{E}_0 = W + 0{\cdot}238$$
$$E_1 + \overline{E}_0 = W + 0{\cdot}222 \qquad E_0 + \overline{E}_1 = W + 0{\cdot}238$$

The fact that the third and the fourth level have the same energy, together with the fact that the spectrum of diphenyl sulphide shows a single band in the region corresponding to the particular transition, seems to justify our mode of calculating the perturbations for the second benzene ring.

From the previous values we obtain for the corresponding transitions the following values :

	Calc.	Found
I	4·72 e.v. (2640 Å)	2700 Å
II and III	4·95 e.v. (2500 Å)	2500 Å

As for the weights of the various structures in the various excited levels, they are obtained by multiplication of the relative weights corresponding to the two partial problems.

The first transition is therefore essentially due to a structure of conjugated type, while the second and the third transition, which coincide, form a single band which can be considered a modified benzene band.

Conclusions.—The fundamental fact emerging from our calculation is the following: the band towards the longer wavelength in anisole is essentially due to a transition of type B_{2u} in benzene, although modified, while the band in the 220 mμ region is essentially a transition of type B_{1u} modified. On the other hand, in thioanisole the band in the 250 mμ region is still of the type B_{2u} modified, while the absorption in the 280 mμ region is a new transition due to the interaction of the $3p$ electrons of sulphur with the phenyl ring; *i.e.*, the interaction $\overbrace{\ddot{S}\text{–Ph}}$ in thioanisole is much stronger than that of $\overbrace{\ddot{O}\text{–Ph}}$ in anisole.

A similar situation to that in thioanisole occurs in diphenyl sulphide, where the maximum in the 275 mμ region is essentially due to the $\pi_8{}^8$ chromophore, as empirically assigned by one of us from an ultraviolet spectral study; it also follows from our previous calculation that the second phenyl group of diphenyl sulphide, compared with that in thioanisole, does not significantly affect the excitation energy.

This work has benefited from a grant from the Italian C.N.R. The authors are indebted to Professor Coulson for helpful discussions and for criticism of this paper.

Dept. of Industrial Chemistry,
University of Bologna.

[*Received, June 19th,* 1956.]

964. *Coenzyme A. Part X.* Model Experiments on the Synthesis of Pyrophosphates of N-Pantoylamines. New Methods for the Debenzylation of Esters of Pyrophosphoric Acid.*

By J. Arris, J. Baddiley, J. G. Buchanan, and E. M. Thain.

Compounds now prepared in connection with a projected synthesis of 3′-dephospho-coenzyme A (I; R = H) include the 4-phosphate (III; R = H) and 4-pyrophosphate (V; R = H) of *N*-pantoyl*cyclo*hexylamine. The pyrophosphate was prepared from the 4-phosphate or its monobenzyl ester (III; R = CH_2Ph) by reaction with dibenzyl phosphorochloridate, followed by reduction.

Benzyl groups were readily removed from esters of pyrophosphoric acid and from nucleotides by reduction with sodium in liquid ammonia. Dibenzyl pyrophosphate gave inorganic pyrophosphate in high yield, tribenzyl pyrophosphate gave mainly pyrophosphate, and tetrabenzyl pyrophosphate gave mainly orthophosphate.

Some benzyl esters of ortho- and pyro-phosphoric acid are also debenzylated in alcoholic solution by irradiation with ultraviolet light.

There are several general procedures which might be applicable to the synthesis of coenzyme A (I; R = PO_3H_2) or 3′-dephospho-coenzyme A (I; R = H). These all involve condensation of two phosphoric esters, such as adenosine-5′ phosphate and pantetheine-4′ phosphate or their derivatives, to give a pyrophosphate. Reagents which effect similar condensations have been examined by us in model experiments on the synthesis of 3′-dephospho-coenzyme A. The presence of a thiol or sulphide group and of two amide groups in the pantetheine-4′ phosphate component usually interfered with pyrophosphate synthesis, but experiments described in this paper suggest that the pantothenic amide group does not preclude pyrophosphate synthesis through phosphorochloridates.

N-Pantoyl*cyclo*hexylamine (II) was chosen as a model for the introduction of a pyrophosphate group. This amide was readily phosphorylated with dibenzyl phosphorochloridate to give a neutral dibenzyl ester. It was shown earlier that phosphorylation of pantothenic acid derivatives with this reagent gives rise exclusively to 4-phosphates.[1] The neutral ester could not be purified but was hydrogenated catalytically to *N*-pantoyl*cyclo*hexylamine-4 phosphate (III; R = H), characterised as the crystalline mono*cyclo*hexylamine salt. Treating the triethylamine salt of this phosphate with dibenzyl phosphorochloridate and hydrogenating the product gave a mixture. Paper chromatography of the products showed that, besides inorganic ortho- and pyro-phosphates, unchanged *N*-pantoyl*cyclo*hexylamine-4 phosphate, and the 2 : 4-cyclic phosphate[2] (IV), there was a major spot of the required *N*-pantoyl*cyclo*hexylamine-4 pyrophosphate (V; R = H). This component was isolated by extraction from a number of paper chromatograms and converted into its crystalline *cyclo*hexylamine salt. Its structure was proved by analysis and by its conversion into the phosphate (III; R = H) and inorganic phosphate on short acid hydrolysis.

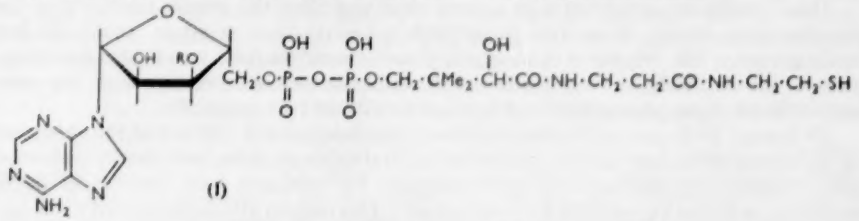
When the dibenzyl ester of *N*-pantoyl*cyclo*hexylamine-4 phosphate was heated with barium thiocyanate in 2-ethoxyethanol,[3] the monobenzyl hydrogen phosphate (III; R = CH_2Ph) was formed. It was isolated as its crystalline *cyclo*hexylamine salt. The triethylamine salt of this monobenzyl ester reacted with dibenzyl phosphorochloridate and the resulting mixture, after removal of benzyl groups by hydrogenation, was examined

* Part IX, *J.*, 1954, 2803.

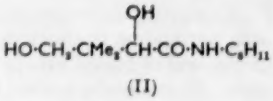
[1] Baddiley and Thain, *J.*, 1953, 1601.
[2] *Idem*, *ibid.*, p. 903.
[3] Morrison and Atherton, B.P. 675,779.

on paper. The products were very similar to those from the unprotected *N*-pantoyl-*cyclo*hexylamine-4 phosphate. A major product, with chromatographic properties identical with those of *N*-pantoyl*cyclo*hexylamine-4 pyrophosphate, was hydrolysed quantitatively to *N*-pantoyl*cyclo*hexylamine-4 phosphate and inorganic phosphate by short acid treatment.

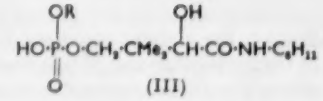
The neutral dibenzyl ester obtained by phosphorylation of *N*-pantoyl*cyclo*hexylamine has interesting properties. Attempts to crystallise it led to the isolation of the *cyclo*hexylamine salt of dibenzyl phosphate. Even with rapid working under conditions as anhydrous as possible, debenzylation with a tertiary base [4] or with barium thiocyanate [3] led to the production of dibenzyl phosphate. The latter has solubilities very similar to those of the required monobenzyl ester and neither repeated crystallisation of the *cyclo*hexylamine salt nor purification through metal salts effected a separation. The presence of dibenzyl phosphate in chromatographically pure preparations of the monobenzyl ester (III; R = CH_2Ph) was shown by catalytic hydrogenolysis when, together with the 4-phosphate, a trace of inorganic phosphate was always produced. We envisage hydrolysis of the neutral ester (owing to its hyroscopic nature) leading to the production of pantolactone and the *cyclo*hexylamine salt of dibenzyl phosphate. We have noticed the formation of diphenyl phosphate and simultaneous fission of the amide linkage with several 4-(*OO*-diphenylphosphoric) esters of pantothenic acid derivatives during either prolonged storage or isolation procedures involving prolonged contact with aqueous solvents.



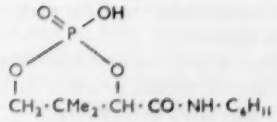
(I)



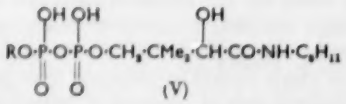
(II)



(III)



(IV)



(V)

The above syntheses suggest that it might be possible to prepare 3′-dephospho-coenzyme A from a suitably protected derivative of pantetheine-4′ phosphate and 2′ : 3′-*iso*propylideneadenosine-5′ benzyl phosphorochloridate.[5] An intermediate in this synthesis would be an unsymmetrical pyrophosphate bearing one or two benzyl groups. The benzyl groups would have to be removed at a later stage in the synthesis. It was also thought that protection of both the 2′-hydroxyl group in the pantoyl residue and the terminal thiol group as their benzyl ethers might be necessary. These partially benzylated esters and ethers could occur in syntheses of the more direct type in which condensing agents such as carbodi-imides,[6] oxime sulphonates,[7] ethoxyacetylene,[8] etc., are used. In several routes, then, the need would arise for the removal under mild conditions of benzyl groups

[4] Cf. Baddiley, Clark, Michalski, and Todd, *J.*, 1949, 815.
[5] Corby, Kenner, and Todd, *J.*, 1952, 3669.
[6] Khorana and Todd, *J.*, 1953, 2254
[7] Atherton, Morrison, Cremlyn, Kenner, Todd, and Webb, *Chem. and Ind.*, 1955, 1183.
[8] Arens and Doornbos, *Rec. Trav. chim.*, 1955, **74**, 79.

from a pyrophosphate. Hitherto, this has been done by catalytic hydrogenolysis,[9] quaternisation with a strong tertiary base,[4] anionic debenzylation,[2, 10, 11] or acid-catalysed transfer of benzyl to phenol.[12] The presence of sulphur in our compounds precluded hydrogenolysis with a palladium or platinum catalyst, and acidic phenol solutions caused extensive decomposition of some of the sulphur-containing model compounds. The former difficulty was overcome in earlier work on the synthesis of simple monophosphates of pantetheine by removing benzyl groups with sodium in liquid ammonia.[1] It was of interest to examine the effect of this reagent on pyrophosphates.

The various compounds were treated with sodium in liquid ammonia under anhydrous conditions and the products, after removal of ammonia by evaporation, were rapidly dissolved in water and passed through a column of a cation-exchange resin in the free acid form. The resulting solution of phosphates was neutralised with ammonia without delay and examined by paper chromatography. P^1P^2-Dibenzyl pyrophosphate was converted quantitatively into inorganic pyrophosphate. Tribenzyl pyrophosphate gave mainly inorganic pyrophosphate but also some orthophosphate. With tetrabenzyl pyrophosphate more orthophosphate was formed but even here a certain proportion of inorganic pyrophosphate was detected. A third product from tetrabenzyl pyrophosphate was recognised as inorganic phosphoramidate. This substance was identical in R_P with inorganic phosphoramidate produced by the action of sodium in liquid ammonia on dibenzyl phosphoramidate.[13]

These results are consistent with general ideas regarding the greater reactivity of the pyrophosphate linkage in neutral pyrophosphoric esters than in esters containing free acidic groups. The formation of inorganic phosphoramidate from tetrabenzyl pyrophosphate is not surprising, since ammonia reacts readily at room temperature with this ester to give dibenzyl phosphoramidate and ammonium dibenzyl phosphate.[14]

P^1-Benzyl P^2-*N*-pantoyl*cyclo*hexylamine-4 pyrophosphate (V; R = CH_2Ph), prepared by the action of barium thiocyanate on the neutral tribenzyl ester, was readily converted into *N*-pantoyl*cyclo*hexylamine-4 pyrophosphate by reduction with sodium in liquid ammonia, as well as by catalytic hydrogenolysis. This reagent also debenzylated 2′ : 3′-*iso*propylideneadenosine-5′ dibenzyl phosphate to 2′ : 3′-*iso*propylideneadenosine-5′ phosphate. Although the method could not be used with pyrimidine nucleotides because of reduction of the pyrimidine ring,[15] it is useful for the removal of benzyl groups from intermediates in many nucleoside pyrophosphate syntheses. It is already known that benzyl groups on the 2′-hydroxyl and the thiol group in pantetheine and its phosphates are removed under the conditions of reduction described above.[1]

Although complete removal of benzyl groups from a fully benzylated derivative of 3′-dephospho-coenzyme A by sodium in liquid ammonia would proceed in low yield, reasonable yields should be obtained from partially benzylated derivatives.

The relative ease of removal of benzyl as opposed to other alkyl and aryl groups by various techniques is sometimes attributable to the ready formation of benzyl radicals. This suggested to us the possibility of debenzylating pyrophosphates by irradiation with ultraviolet light. Dibenzyl phosphate and tetrabenzyl pyrophosphate were debenzylated smoothly in alcoholic solution by ultraviolet light, the latter giving inorganic pyrophosphate accompanied by only traces of orthophosphate. Adenosine-5′ benzyl phosphate, on the other hand, was completely unaffected under the experimental conditions employed. This relative stability is probably due to the strong absorption of ultraviolet light by the purine moiety.

[9] Baddiley and Todd, *J.*, 1947, 648.
[10] Clark and Todd, *J.*, 1950, 2023, 2031.
[11] Anand, Clark, Hall, and Todd, *J.*, 1952, 3665.
[12] Christie, Kenner, and Todd, *J.*, 1954, 46.
[13] Baddiley, Buchanan, and Letters, *J.*, 1956, 2812.
[14] Atherton and Todd, *J.*, 1947, 674.
[15] Burke, *Chem. and Ind.*, 1954, 1393.

Experimental

Evaporations were carried out *in vacuo*.

*N-Pantoyl*cyclo*hexylamine*.—DL-Pantolactone (7 g.), dissolved in *cyclo*hexylamine (*ca.* 50 c.c.), was refluxed for 30 min. Solvent was removed and a little ether was added. After decantation of the ether, the solid residue of *amide* recrystallised from aqueous alcohol as prisms, m. p. 111° (10 g., 80%) (Found: C, 62·8; H, 9·8; N, 6·3. $C_{12}H_{23}O_3N$ requires C, 62·8; H, 10·0; N, 6·1%).

A sample prepared from D(−)-pantolactone had m. p. 104°, $[\alpha]_D$ +51·4° (*c* 2·57 in EtOH) (Found: C, 62·6; H, 10·2; N, 6·1%).

cyclo*Hexylammonium Salt of* DL-N-*Pantoyl*cyclo*hexylamine*-4 *Phosphate*.—Dry DL-pantoyl-*cyclo*hexylamine (5·0 g.) was dissolved in dry pyridine (30 c.c.) and cooled in acetone–carbon dioxide. To the slurry was added dibenzyl phosphorochloridate (from 5·5 g. of dibenzyl phosphite) in carbon tetrachloride (5 c.c.). The mixture was allowed to reach room temperature and after an hour was treated with the same amount of the phosphorochloridate under identical conditions. After 2 days at −10° pyridine was removed by distillation. The syrup was dissolved in ethyl acetate (20 c.c.) and washed successively with water, 2N-sulphuric acid, and water. The solution was dried ($MgSO_4$), filtered, and evaporated to a clear syrup (15·7 g.).

A portion (10·0 g.) was hydrogenated in ethanol with palladium as catalyst. The catalyst was filtered off, water was added, and the ethanol evaporated. The solution was adjusted to pH8 with barium hydroxide solution, barium phosphate was filtered off, and the solution was passed through a column of Amberlite IR-120 (H^+ form) to remove barium ions. The effluent and aqueous washings were neutralised with *cyclo*hexylamine and evaporated to dryness. Trituration with ethanol gave a solid (8·8 g., 79%) which could not be recrystallised, although paper chromatography indicated that it was homogeneous. However, the *mono*cyclo*hexylamine salt*, m. p. 194—195°, readily crystallised from water (Found: C, 53·2; H, 9·1; N, 7·1; P, 7·7. $C_{18}H_{37}O_6N_2P$ requires C, 53·0; H, 9·1; N, 6·9; P, 7·6%) and gave one spot when chromatographed on paper in *n*-propyl alcohol–ammonia (see Table).

cyclo*Hexylammonium Salt of Benzyl* N-*Pantoyl*cyclo*hexylamine*-4 *Phosphate*.—D-*N*-Pantoyl*cyclo*hexylamine (11·5 g.) was phosphorylated with dibenzyl phosphorochloridate (from 15·0 g. of dibenzyl phosphite) in the usual way. The mixture, after evaporation of excess of pyridine, was dissolved in ether and washed exhaustively with water, N-sulphuric acid, water, N-sodium hydroxide, and finally water, dried ($MgSO_4$), and evaporated to a syrup (22·7 g.). Paper chromatography showed the absence of dibenzyl phosphate. The neutral ester was dissolved in 2-ethoxyethanol (100 c.c.), and barium thiocyanate (25 g.) added. The mixture was heated at 100° for 1 hr., during which it solidified. The following day it was treated with ether (500 c.c.) and filtered, and the solid was washed with ether and dried (P_2O_5). The product (37 g.), dissolved in 50% aqueous ethanol (400 c.c.), was poured through a column (2·7 × 90 cm.) of Amberlite IR-120 (H^+ form). Washing of the column was continued until the effluent was neutral, and the combined effluent was adjusted to pH 8 with *cyclo*hexylamine (*ca.* 13 c.c.). The solution was evaporated to 300 c.c. and the crystalline product was filtered off and washed with acetone and ether (15 g.; m. p. 189—190°). A further crop (1·0 g.; m. p. 183°) was obtained from the mother-liquors. Recrystallisation of the first crop from ethanol–ether lowered the m. p., but two crystallisations from water yielded a cyclo*hexylamine salt* with m. p. 190—191° (Found: C, 60·2; H, 8·7; N, 5·8; P, 6·3. $C_{30}H_{43}O_6N_2P$ requires C, 60·3; H, 8·6; N, 5·6; P, 6·2%).

Hydrogenolysis of the Monobenzyl Ester.—The above *cyclo*hexylamine salt (m. p. 190°; 0·5 g.) was hydrogenolysed in aqueous-alcoholic solution with palladium. Paper chromatography of the products in *n*-propyl alcohol–ammonia–water showed a strong spot identical with that from *N*-pantoyl*cyclo*hexylamine-4 phosphate, together with a trace of inorganic phosphate. Evaporation of the solution after removal of catalyst, followed by crystallisation from water, gave the mono*cyclo*hexylamine salt, m. p. 191—193°.

N-*Pantoyl*cyclo*hexylamine*-4 *Pyrophosphate*.—(a) *From* N-*pantoyl*cyclo*hexylamine*-4 *phosphate*. The mono*cyclo*hexylamine salt (0·5 g.) was converted into the free acid by passage through Amberlite IR-120 (H^+). The effluent was neutralised with triethylamine and evaporated to dryness. The water was evaporated and the residue dissolved in methyl cyanide (5 c.c.) and chloroform (10 c.c.). The solution was evaporated to dryness and the process was repeated, both chloroform and toluene being used. The residue crystallised. It was dissolved

in a mixture of dry methyl cyanide (3 c.c.) and carbon tetrachloride (5 c.c.) and cooled to −10°. To this solution was added dibenzyl phosphorochloridate (from 0·32 g. of dibenzyl phosphite; 1·1 mol.) and the whole was kept at 0° for 2·5 hr., then evaporated to dryness at 0°. The residue, dissolved in ethanol (96%), was hydrogenolysed in the presence of palladium black. Paper chromatography showed the formation of several compounds including inorganic ortho- and pyro-phosphate. A major spot having an R_P value slightly lower than that of *N*-pantoyl-*cyclo*hexylamine-4 phosphate in the *iso*butyric acid–ammonia solvent was extracted from a chromatogram and shown to be hydrolysed completely by N-hydrochloric acid in 7 min. at 100° to inorganic phosphate and *N*-pantoyl*cyclo*hexylamine-4 phosphate. This compound was stable to hydrolysis in aqueous ammonia (*d* 0·88) under the same conditions. It was isolated by running as bands on Whatman No. 3 paper, first in *n*-propyl alcohol–ammonia–water (6 : 3 : 1) followed by *n*-butyl alcohol–acetic acid–water. It was converted into its *cyclo*hexylamine salt (42 mg.) by the usual ion-exchange procedure (see above), then further purified through the mercury salt and reconverted into the *dicyclohexylamine salt*, m. p. 130° (with previous shrinking) (Found: C, 49·5; H, 9·9; N, 8·3; P, 8·3. $C_{30}H_{64}O_9N_4P_2,2H_2O$ requires C, 49·8; H, 9·4; N, 7·8; P, 8·6%).

(b) *From benzyl* N-*pantoyl*cyclo*hexylamine*-4 *phosphate.* The *cyclo*hexylamine salt of the DL-monobenzyl ester (m. p. 189°) was treated with ether (10 c.c.) and 2N-sulphuric acid (10 c.c.), and then the ether layer was removed. After two further ether-extractions the combined extracts were dried (Na_2SO_4) and filtered, and triethylamine (0·2 c.c.) was added. The solution was evaporated to dryness, finally with chloroform and toluene. The residue was dissolved in dry chloroform (5 c.c.), and dibenzyl phosphorochloridate (from 0·27 g. of dibenzyl phosphite) in chloroform (15 c.c.) added. Triethylamine (1 drop) was added and the solution was left at room temperature for 2 hr. Evaporation left a semicrystalline gum which was rapidly dissolved in 95% ethanol and hydrogenolysed (palladium black). Hydrogen uptake was complete in 15 min. The catalyst was removed and the solution neutralised with ammonia, concentrated, and examined by paper chromatography.

The chromatographic analysis (in *n*-propyl alcohol–ammonia–water) was very similar to that given by the crude product obtained as in method (a). The material in the *N*-pantoyl-*cyclo*hexylamine-4 pyrophosphate spot, which was present in slightly greater amount than before, was readily hydrolysed by N-hydrochloric acid in 7 min. at 100°, to give *N*-pantoyl-*cyclo*hexylamine-4 phosphate and inorganic phosphate.

P^1-*Benzyl* P^2-(N-*Pantoyl*cyclo*hexylamine*-4) *Pyrophosphate.*—The neutral tribenzyl pyrophosphoric ester was prepared from the D-monobenzyl ester (0·5 g. of *cyclo*hexylamine salt, m. p. 190°) as in (b) above. The chloroform solution was evaporated to dryness and the residue dissolved in 2-ethoxyethanol (5 c.c.). Dry barium thiocyanate (1 g.) and triethylamine (1 drop) were added, and the mixture was heated at 100° for 15 min., then cooled. Light petroleum (b. p. 40—60°; 45 c.c.) was added, the mixture shaken, and the petroleum layer removed and discarded. Ether (50 c.c.) was added, whereupon a solid separated. The ether layer was decanted, the solid was washed with more ether (50 c.c.), and the ether extracts were discarded. The solid was ground with water (10 c.c.) and ether (10 c.c.) and filtered. The precipitate was washed successively with water (15 c.c.), acetone (10 c.c.), and ether. After drying, it was obtained as a pale yellow-green powder A (0·22 g.). The combined filtrates were evaporated to dryness, finally with benzene. The residual solid was triturated with acetone, filtered, and washed with acetone and then ether, to give a white powder B (0·27 g.).

Paper chromatography of product A in *n*-propyl alcohol–ammonia–water showed the presence of P^1P^2-dibenzyl pyrophosphate, some unchanged monobenzyl ester, and a spot with and R_P between these which was apparently the required compound. Solid B contained a small amount of the cyclic phosphate of *N*-pantoyl*cyclo*hexylamine together with unchanged monobenzyl ester. Dibenzyl phosphate would have the same R_P as the monobenzyl ester of *N*-pantoyl*cyclo*hexylamine-4 phosphate.

Product A (60 mg.) was converted into the free acid by treatment with Amberlite IR-120 (H^+ form) and hydrogenolysed in 50% aqueous ethanol over palladium black. The product, after removal of catalyst, was neutralised with ammonia and run on paper in *n*-propyl alcohol–ammonia–water. Together with inorganic ortho- and pyro-phosphate and *N*-pantoyl*cyclo*-hexylamine-4 phosphate, was a major spot of *N*-pantoyl*cyclo*hexylamine-4 pyrophosphate, identified by its R_P value and ready hydrolysis with acid to the monophosphate and inorganic orthophosphate.

Products A (100 mg.) and B (100 mg.) were treated with sodium in liquid ammonia by the method described below for benzyl pyrophosphates. Chromatograms of the neutralised products showed that product A gave the same compounds as were obtained by catalytic hydrogenolysis. Product B yielded mainly the 4-phosphate together with some inorganic phosphate, cyclic phosphate, and a trace of the 4-pyrophosphate (characterised by acid hydrolysis as before).

Debenzylation of Pyrophosphoric Esters with Sodium in Liquid Ammonia.—Small pieces of sodium were added to the appropriate ester (0·001 mole) in liquid ammonia (50 c.c.) under anhydrous conditions until a permanent blue colour was obtained. After addition of a few drops of alcohol the solution was allowed to evaporate. Last traces of ammonia were evaporated and the residue was rapidly dissolved in water (20 c.c.), the dibenzyl filtered off, and the filtrate passed through Amberlite IR-120 (H^+ form). The effluent and aqueous washings of the column were neutralised with 2N-sodium hydroxide, and aliquot parts were examined by paper chromatography in *n*-propyl alcohol–ammonia–water (6 : 3 : 1). The product from P^1P^2-dibenzyl pyrophosphate showed the presence of only inorganic pyrophosphate, while the products from the other two esters showed that inorganic orthophosphate had been produced. The latter products were analysed for inorganic phosphate and total phosphate by Allen's method, the pyrophosphate being calculated by difference. Tetrabenzyl pyrophosphate yielded orthophosphate 76·2% and pyrophosphate 9·7%; for tribenzyl pyrophosphate the values were 22·2 and 58·7% respectively. The product from tetrabenzyl pyrophosphate gave a spot on chromatography corresponding to phosphoramidic acid which would behave on analysis as inorganic orthophosphate.

The debenzylation of 2′ : 3′-*iso*propylideneadenosine-5′ dibenzyl phosphate was carried out similarly. Amberlite IR-120 (ammonium form) was used in this case for the removal of sodium ions. The main product was 2′ : 3′-*iso*propylideneadenosine-5′ phosphate. Smaller amounts of unidentified products were also formed.

Action of Ultraviolet Light on Benzyl Phosphates.—Dibenzyl phosphates. Dibenzyl phosphate (50 mg.) in (*a*) dry ethanol (2 c.c.) and (*b*) 50% aqueous ethanol (2 c.c.) was irradiated in silica flasks by a " Mineralite " lamp, dry oxygen-free nitrogen being bubbled through the solutions. Aliquot parts were withdrawn at intervals and examined by paper chromatography in the *iso*butyric acid–ammonium *iso*butyrate solvent. In each case inorganic phosphate (R_P 0·37) and benzyl hydrogen phosphate (R_P 0·85) were produced from the starting material (R_P 0·93).

R_P values of phosphoric and pyrophosphoric esters of N*-pantoylcyclohexylamine.*

	R_P in PrⁿOH–aq. NH_3 (d 0·88)–H_2O	
	6 : 3 : 1	8 : 1 : 1
Pyrophosphate	0·08	0·0
Orthophosphate	0·17	0·02
Phosphoramidate	0·18	—
N-Pantoyl*cyclo*hexylamine-4 phosphate	0·67	0·29
N-Pantoyl*cyclo*hexylamine-4 pyrophosphate	0·56	0·16
N-Pantoyl*cyclo*hexylamine-2 : 4 phosphate	0·88	0·79
N-Pantoyl*cyclo*hexylamine-4 benzyl phosphate	0·93	0·92
P^1-Benzyl P^2-(*N*-pantoyl*cyclo*hexylamine-4) pyrophosphate	0·81	—
Dibenzyl phosphate	0·93	0·86
Dibenzyl pyrophosphate	0·77	0·60
Tribenzyl pyrophosphate	—	0·90

Tetrabenzyl pyrophosphate. The ester (0·2 g.) was dissolved in dry ethanol (10 c.c.) and nitrogen was passed through the solution in a silica flask. The solution was irradiated as before and samples were withdrawn at intervals and examined by paper chromatography. After 7 hr. there was a strong spot of inorganic pyrophosphate and only a trace of orthophosphate. Spots of intermediate benzyl esters of pyrophosphoric acid were detected.

Ultraviolet irradiation under these conditions had no effect on *S*-benzylcysteine or adenosine-5′ benzyl phosphate.

We thank the Nuffield Foundation and the Department of Scientific and Industrial Research for financial support. One of us (E. M. T.) held an I.C.I. Fellowship in the University of London when this work was started at the Lister Institute of Preventive Medicine.

KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE UPON TYNE.

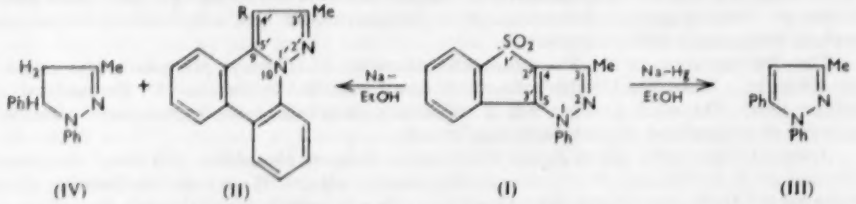
[*Received, July 9th,* 1956.]

965. *A Molecular Rearrangement during the Reduction of Thionaphthenopyrazole Dioxides.*

By W. J. Barry, I. L. Finar, and Alma B. Simmonds.

Reduction of 3-methyl-1-phenylthionaphtheno(2′ : 3′-4 : 5)pyrazole 1′ : 1′-dioxide (I) with sodium in ethanol causes an intramolecular rearrangement with the formation of 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine (II; R = H). The structure of this compound has been ascertained through synthesis.

3-Methyl-1-phenylthionaphtheno(2′ : 3′-4 : 5)pyrazole 1′ : 1′-dioxide (I) (previously referred to as 3-methyl-1-phenyl-4 : 5-thionaphthenopyrazole-1′ : 1′-dioxide [1]), when treated with sodium amalgam in ethanol, undergoes simple fission to 3-methyl-1 : 5-diphenylpyrazole [2] (III). When, however, metallic sodium in boiling ethanol is the reagent, the main product is 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine-4′-sulphinic acid (II; R = SO_2H) which separates from the reaction mixture as the sodium salt; a small amount of 3-methyl-1 : 5-diphenyl-Δ^2-pyrazoline (IV) is also formed.[2]

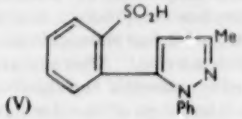


(IV) (II) (I) (III)

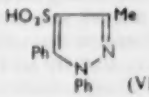
The free sulphinic acid (II; R = SO_2H) is very unstable in aqueous solution, especially in the presence of hydrochloric acid, sulphur dioxide being evolved with the formation of 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine (II; R = H) (previously [2] referred to as compound A). Sulphinic acids which undergo loss of sulphur dioxide usually require a higher temperature for the reaction.[3] Although the sodium salt is stable in alkaline solution, it does not react with benzyl chloride to give a sulphone, but is recovered unchanged after long heating with this reagent. These properties show that this sulphinic acid is different from 3-methyl-1-phenyl-5-pyrazolylbenzene-*o*-sulphinic acid (V) which is readily benzylated and is only slowly decomposed by cold hydrochloric acid.[4] To account for this one might assume that fission of the C–S bond in the original thionaphthenopyrazole dioxide (I) occurs on the side adjacent to the benzene ring, to form 3-methyl-1 : 5-diphenylpyrazole-4-sulphinic acid (VI); the latter was therefore synthesised as follows. Di-(3-methyl-1 : 5-diphenyl-4-pyrazolyl) disulphide, prepared by a modification of Vaillant's method,[5] was reduced to the thiol with sodium dithionite, then benzylated, and the benzyl sulphide was oxidised with hydrogen peroxide in acetic acid to 3-methyl-1 : 5-diphenyl-4-toluene-ω-sulphonylpyrazole (VI; $Ph{\cdot}CH_2{\cdot}SO_2$ instead of SO_2H). This sulphone, on reductive fission with sodium amalgam [6] and subsequent acidification, gave the sulphinic acid (VI). This compound was characterised by its reactions and by benzylation to regenerate the sulphone. Like its isomer (V), it slowly lost sulphur dioxide in the presence of hydrochloric acid to give 3-methyl-1 : 5-diphenylpyrazole (III).[4] Further reduction of the sulphinic acid (VI) with metallic sodium in ethanol gave the thiol (VI; SH instead of SO_2H) and a small quantity of an oil which appeared to be 3-methyl-1 : 5-diphenylpyrazoline (IV).

[1] Barry, Thesis, London, 1933.
[2] Barry and McClelland, *J.*, 1935, 471.
[3] Gessner, *Ber.*, 1876, **9**, 1500.
[4] Barry and Finar, *J.*, 1954, 138.
[5] Vaillant, *Compt. rend.*, 1894, **119**, 647.
[6] Dabby, Kenyon, and Mason, *J.*, 1952, 4881.

These results exclude the possibility that 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine (II; R = H) is formed by rearrangement after the loss of sulphur dioxide from the sulphinic acid (V) or (VI). The sulphinic acid (II; R = SO_2H) must be formed by a rearrangement during the initial reduction of the thionaphthenopyrazole dioxide. In view of the structure of the sulphinic acid (II; R = SO_2H), it must be formed by rupture of the C–S bond on the side adjacent to the benzene ring, followed by a rotation of this ring



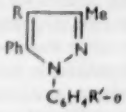
(V)



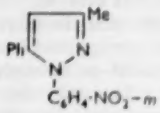
(VI)

about the remaining bond, and the formation of a new bond with the *ortho*-position of the *N*-phenyl nucleus. It is not clear at present whether the mechanism involves free-radical formation, induced by the metallic sodium, or whether the reducing conditions and the presence of hydrogen are necessary. The sodium ethoxide may also play a part.

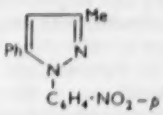
Attempts to degrade the phenanthridine (II; R = H) have proved fruitless so far, the compound being resistant to all reducing or oxidising agents except acid dichromate or acid permanganate which destroy it.[2,7] It was thought, however, that the pyrazole nucleus might be weakened towards oxidising agents by the introduction of a hydroxyl group as follows. The sodium sulphinate (II; R = SO_2Na) gave, with sodium hypochlorite, a sulphonyl chloride (II; R = SO_2Cl). At this stage came the first direct evidence that the sulphinic acid group is in the reactive (4′) position of the pyrazole nucleus, since the sulphonyl chloride did not react with bromine in organic solvents. 3′-Methylpyrazolo(5′ : 1′-9 : 10)phenanthridine itself is very reactive towards electrophilic reagents, which preferentially attack the 4′-carbon atom in all cases.[7] Fusion of the corresponding sulphonic acid (II; R = SO_3H) with alkali gave, instead of the expected hydroxy-compound, the original 3′-methylpyrazolophenanthridine (II; R = H) by removal of the sulphonic acid group. The sulphonic acid was also hydrolysed in aqueous solution, slowly in the cold, rapidly on warming. Oxidation experiments with the sulphonic acid gave either unchanged material or unworkable tars.



(VII)



(VIII)



(IX)

With the failure to obtain analytical evidence for the structure of the nucleus (II), attention was turned to synthesis. 1-*o*-Aminophenyl-3-methyl-5-phenylpyrazole (VII; R = H, R′ = NH_2) was prepared by condensation of benzoylacetone with *o*-nitrophenylhydrazine, and reduction of the product with zinc and hydrochloric acid. The diazotised amine lost nitrogen on treatment with hypophosphorous acid, giving 3′-methylpyrazolo-(5′ : 1′-9 : 10)phenanthridine (II; R = H), whereas a simple deamination would have given methyldiphenylpyrazole.

Next, the nitro-compound (VII; R = H, R′ = NO_2) was brominated, to give the 4-bromo-derivative (VII; R = Br, R′ = NO_2), then reduced to the amine, and the diazotised amine was treated with hypophosphorous acid, giving 4′-bromo-3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine (II; R = Br). Reduction and deamination of the isomeric nitro-compounds (VIII and IX) gave only 3-methyl-1 : 5-diphenylpyrazole.

Experimental

3-Methyl-1-phenylthionaphtheno(2′ : 3′-4 : 5)pyrazole 1′ : 1′-Dioxide.—Condensing dithiosalicylic acid with acetylacetone in concentrated sulphuric acid at 45—50°, leaving the mixture

[7] Smith, Thesis, London, 1939.

overnight, and running it slowly into ice-cold water with stirring gave an almost quantitative yield of nearly pure 2-acetyl-3-hydroxythionaphthen.[8] The crude pyrazole, obtained by condensation with phenylhydrazine hydrochloride, was oxidised to the dioxide, which has now been observed to crystallise in two modifications, m. p. 180° and m. p. 187°, with a transition temperature at about 180°. Recrystallisation of the higher-melting modification regenerates that of m. p. 180°, while keeping this for several months causes the m. p. to rise.

Di-(1-benzoylacetonyl) Disulphide (*αα'-Dithiobenzoylacetone*).—Chloroform (180 c.c.) (dried over Na_2SO_4 for 12 hr.), containing copper benzoylacetone (38·5 g.), was dried for a further hour over the same reagent, filtered, and cooled to 0°. Sulphur monochloride (8 c.c.) in chloroform (25 c.c.) was added dropwise to this solution with stirring. After removal of excess of sulphur monochloride with a stream of dry air (2 hr.), evaporation of the chloroform gave a reddish oil (23 g., 60%) which on recrystallisation from ethanol gave the disulphide, m. p. 112—114°. Vaillant [5] obtained only a 30% yield.

Di-(3-methyl-1:5-diphenyl-4-pyrazolyl) Disulphide.—Dithiobenzoylacetone (33 g.; 1 mol.) and phenylhydrazine (16 g., 2 mols.) were heated in glacial acetic acid (200 c.c.) for 1 hr. at 100°. After some hours the solution deposited crystals of the pyrazole (27 g., 58%). Recrystallisation from butan-1-ol gave lemon-yellow crystals m. p. 204° (Vaillant [5] gave m. p. as 162°) (Found: C, 72·5; H, 4·6; N, 10·4; S, 12·1. Calc. for $C_{38}H_{34}N_4S_2$: C, 72·4; H, 4·9; N, 10·6; S, 12·2%).

4-Benzylthio-3-methyl-1:5-diphenylpyrazole.—The preceding disulphide (16 g.) was boiled with ethanol (200 c.c.) and water (400 c.c.) containing sodium dithionite (50 g.) and sodium hydroxide (10 g.). After 1½ hr. the almost clear solution was treated with benzyl chloride (10 c.c.) with shaking, and the mixture heated on the steam-bath for ½ hr. At 0° the *benzyl derivative* separated (14 g., 80%), and formed colourless crystals, m. p. 108°, from ethanol (Found: S, 9·4. $C_{29}H_{26}N_2S$ requires S, 9·0%).

3-Methyl-1:5-diphenyl-4-toluene-ω-sulphonylpyrazole.—The benzyl sulphide (1·5 g.) was dissolved in glacial acetic acid (10 c.c.), and hydrogen peroxide (5 c.c.; 100-vol.) added. After 1 hr. at 100° addition of water precipitated the *sulphone* (1·3 g.) which recrystallised from ethanol as colourless needles, m. p. 162° (Found: C, 70·8; H, 5·2; N, 7·1; S, 8·4. $C_{23}H_{20}O_2N_2S$ requires C, 71·1; H, 5·2; N, 7·2; S, 8·2%).

Reduction of the Sulphone.—The preceding compound (2 g.) was heated in boiling absolute ethanol (50 c.c.) with sodium amalgam (50 g., 5%) for 5—6 hr. After evaporation the yellowish residue (which gave a Smiles sulphinic acid test with anisole and concentrated sulphuric acid) was dissolved in water, and the solution acidified with 3N-hydrochloric acid. The precipitate rapidly became oily and sulphur dioxide was evolved. After being heated for 1 hr. at 100° the residual oil was extracted with chloroform, and the solution dried (Na_2SO_4) and treated with a solution of bromine in chloroform. The precipitated bromo-derivative was recrystallised from ethanol. Its m. p. (72°) was not depressed on admixture with authentic 4-bromo-3-methyl-1:5-diphenylpyrazole (m. p. 73—74°). The reduction with sodium amalgam was repeated with a further quantity of sulphone, the residue after evaporation of the ethanol was dissolved in water (charcoal), and the solution was heated for a few minutes on the steam-bath. Cooling to 0° and careful addition of hydrochloric acid gave a white precipitate of the 3-methyl-1:5-diphenylpyrazole-4-sulphinic acid (Smiles test). A drop of the ethanolic solution from the sodium amalgam reduction gave an intense carmine colour in Knorr's pyrazoline test.

Benzylation of the Sulphinic Acid.—The white precipitate from the last experiment was dissolved in dilute ethanolic potassium carbonate solution, and excess of benzyl chloride added. After 1½ hours' heating at 100° addition of water gave a precipitate of the sulphone which, recrystallised from ethanol had m. p. 162°, not depressed by admixture with 3-methyl-1:5-diphenyl-4-toluene-ω-sulphonylpyrazole.

Reduction of the 3-Methyl-1:5-diphenylpyrazole-4-sulphinic Acid.—The sulphinic acid (0·2 g.) was heated in sodium ethoxide solution (25 c.c.; 5%) for 2 hr. during which sodium (5 g.) was added. The mixture was diluted with water and extracted with ether. Evaporation of the ether gave an oil which gave an intense carmine colour in Knorr's pyrazoline test. The aqueous layer, on acidification with dilute hydrochloric acid and warming to 100°, slowly deposited a white solid, which on recrystallisation from ethanol melted at 200° alone or mixed with di-(3-methyl-1:5-diphenyl-4-pyrazolyl) disulphide.

4'-Chlorosulphonyl-3'-methylpyrazolo(5':1'-9:10)phenanthridine.—Sodium 3'-methylpyrazolo(5':1'-9:10)phenanthridine-4'-sulphinate (sodium sulphinate of compound A) (7 g.), prepared by Barry and McClelland's method,[3] was dissolved in warm 0·5N-sodium hydroxide

(100 c.c.) and filtered. 10% Sodium hypochlorite solution (50 c.c.) was slowly added with shaking. After standing, the precipitate of sulphonyl chloride was cream-coloured and granular (5 g.). Recrystallised from acetone, the *sulphonyl chloride* melted at 165° (Found: C, 57·6; H, 3·3; N, 9·1; S, 9·8; Cl, 11·0. $C_{16}H_{11}O_3N_3ClS$ requires C, 58·0; H, 3·3; N, 8·5; S, 9·7; Cl, 10·7%).

Reduction of the Sulphonyl Chloride.—The sulphonyl chloride (0·5 g.) was heated in ethanol with 5% sodium amalgam (10 g.). The white precipitate which was formed in a few minutes was treated with 3N-hydrochloric acid and, when evolution of sulphur dioxide had ceased, the residual oily solid was recrystallised from dilute ethanol. It then melted at 122° alone or mixed with 3-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine (compound A).

Hydrolysis of the Sulphonyl Chloride.—The sulphonyl chloride (1 g.), suspended in ethanol (100 c.c.), was treated with 50% aqueous potassium hydroxide (20 c.c.) with shaking. The sulphonyl chloride dissolved, and crystals of the potassium sulphonate were deposited.

Alkali Fusion of Potassium 3′-Methylpyrazolo(5′ : 1′-9 : 10)phenanthridine-4′-sulphonate.—Several fusions, in a nickel crucible, of the potassium sulphonate with potassium hydroxide–sodium hydroxide (1 : 1) in air or in nitrogen gave, in all cases, a white sublimate, m. p. 120° [120—124° when mixed with 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine].

Hydrolysis of 3′-Methylpyrazolo(5′ : 1′-9 : 10)phenanthridine-4′-sulphonic Acid.—Acidification of a solution of the above potassium salt gave a clear solution, which, at room temperature, slowly deposited crystals, m. p. 123° alone or mixed with 3′-methylpyrazolo(5′ : 1′-9 : 10)phenanthridine. The hydrolysis was rapid when the acidified solution was warmed. The filtrate from the deposited crystals gave a test for sulphate (barium chloride).

Conversion of the Salt into the Chloride.—The dry potassium sulphonate (0·5 g.) was warmed with excess of phosphorus pentachloride (1 min.), and the oily residue extracted with acetone. After two recrystallisations from acetone, the chloride had m. p. and mixed m. p. 163°.

3-*Methyl*-1-*o*-*nitrophenyl*-5-*phenylpyrazole.*—Benzoylacetone (3·1 g.), heated with *o*-nitrophenylhydrazine (2·9 g.) in ethanol (50 c.c.) and concentrated sulphuric acid (6 c.c.) on a steam-bath for 30 min., gave the *pyrazole* (5·1 g., 96%) as pale yellow crystals, m. p. 104° (from ethanol) (Found: C, 68·6; H, 4·8; N, 14·4. $C_{16}H_{13}O_2N_3$ requires C, 68·6; H, 4·8; N, 15·0%).

3-*Methyl*-1-m-*nitrophenyl*-5-*phenylpyrazole.*—Benzoylacetone (6·6 g.), heated with *m*-nitrophenylhydrazine hydrochloride (9·5 g.) in acetic acid on a steam-bath for 1 hr., gave on dilution with water the *pyrazole* (9·0 g., 64%) as pale yellow crystals, m. p. 118° (from ethanol) (Found: N, 15·3%).

3-*Methyl*-1-p-*nitrophenyl*-5-*phenylpyrazole.*—Benzoylacetone (2 g.) and *p*-nitrophenylhydrazine (2·1 g.) in ethanol on a steam-bath for 2 hr. gave the pyrazole (2·5 g., 70%), m. p. 100°.[9, 10]

1-*Aminophenyl*-3-*methyl*-5-*phenylpyrazoles.*—The nitro-compound in glacial acetic acid was heated with zinc and concentrated hydrochloric acid until colourless. The amine was extracted with ether from the solution made alkaline with concentrated ammonia solution, and recrystallised from ethanol. The *o*-nitro-compound (2·25 g.) gave 1-(*o*-*aminophenyl*-3-*methyl*-5-*phenylpyrazole* (1·8 g., 90%), m. p. 134° (Found: C, 76·7; H, 6·0; N, 16·3. $C_{16}H_{15}N_3$ requires C, 77·1; H, 6·0; N, 16·8%). The *m*-nitro-compound (5 g.) gave 1-*m*-nitrophenyl-3-methyl-5-phenylpyrazole (4·15 g., 74%) [*benzoyl derivative*, m. p. 172° (Found: N, 11·5. $C_{23}H_{19}ON_3$ requires N, 11·9%)]. The *p*-nitro-compound (1·4 g.) gave the amine (0·7 g., 56%), m. p. 150° (benzoyl derivative 170°).[10]

4-*Bromo*-3-*methyl*-1-*nitrophenyl*-5-*phenylpyrazoles.*—The pyrazole in glacial acetic acid was treated with bromine at room temperature. Dilution with water gave a yellow precipitate which was dissolved in chloroform and washed with sodium carbonate solution. The chloroform was evaporated and the pale yellow residue recrystallised from ethanol. The *o*-nitro-compound (2 g.) gave the *bromo-derivative* (2·5 g., 98%), m. p. 142° (Found: Br, 22·2. $C_{16}H_{12}O_2N_3Br$ requires Br, 22·3%). The *p*-nitro-compound (2·1 g.) gave the *bromo-derivative* (2·6 g., 100%), m. p. 154° (Found: Br, 21·9%).

1-*o*-*Aminophenyl*-4-*bromo*-3-*methyl*-5-*phenylpyrazole.*—The nitro-compound (0·55 g.), heated in ethanol with 60% hydrazine hydrate solution and Raney nickel, gave colourless crystals of the *amine* (0·2 g., 40%), m. p. 180° (decomp.) (Found: Br, 24·2. $C_{16}H_{14}N_3Br$ requires Br, 24·4%).

[9] Smiles and McClelland, *J.*, 1921, 1815.
[9] Auwers and Stuhlmann, *Ber.*, 1926, **59**, 1054.
[10] Reilly, Daly, and Drumm, *Proc. Roy. Irish Acad.*, 1931, **40**, *B*, 94.

Hypophosphorous Acid Treatment of the Diazotised Amines.—The amine (0·3 g.) was diazotised in concentrated hydrochloric acid with sodium nitrite solution. After 10 min., the solution was poured into 30% hypophosphorous acid (15 c.c.) and set aside overnight. 1-*o*-Aminophenyl-3-methyl-5-phenylpyrazole gave colourless crystals, m. p. 123—124° (from ethanol) alone or mixed with compound A. 1-*o*-Aminophenyl-4-bromo-3-methyl-5-phenylpyrazole gave colourless crystals, m. p. 139° alone or mixed with "bromo-A." 1-*m*-Aminophenyl- and 1-*p*-aminophenyl-3-methyl-5-phenylpyrazole gave 3-methyl-1 : 5-diphenylpyrazole, characterised by its picrate, m. p. 124°,[11] and its bromo-derivative, m. p. 75°.[12,11]

NORTHERN POLYTECHNIC, HOLLOWAY, LONDON, N.7. [*Received, July 20th*, 1956.]

[11] Auwers and Mauss, *Ber.*, 1926, **59**, 611.
[12] Knorr and Blank, *Ber.*, 1885, **18**, 316.

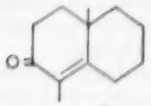
NOTES.

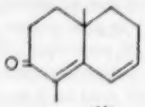
966. *Synthesis of a Dihydrosantonin Isomer.**

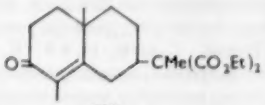
By J. K. CHAKRABARTI, P. DUTT, and P. C. DUTTA.

THIS note reports variations in published methods for the synthesis of santonin D by way of its 1 : 2-dihydro-derivative.

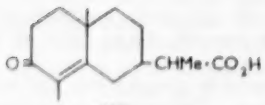
2-Methyl*cyclo*hexanone was condensed in the presence of sodamide with 2-chloroethyl ethyl ketone (instead of with the 2-diethylaminoethyl ketone used by Gunstone and Heggie [1]), and the crude product was refluxed with alkali (this treatment is essential in view of McQuillin's work [2]), giving the ketone (I).


(I)

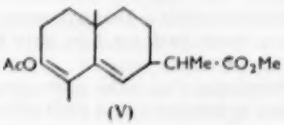

(II)



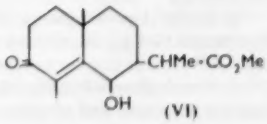
(III)



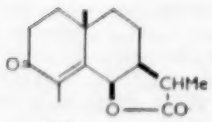
(IV)



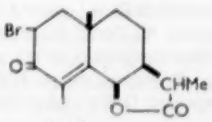
(V)



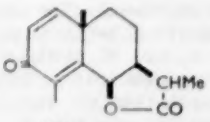
(VI)



(VII)



(VIII)



(IX)

The hexalone (II) was condensed with ethyl methylmalonate in presence of potassium *tert.*-butoxide, but the yield was less than that obtained by Abe *et al.*[3] and our product was contaminated, probably with the ethyl ester of the acid (IV) arising by partial decarboxylation. Hydrolysis and decarboxylation then gives a mixture of acids (IV), separated only by tedious crystallisation; the form isolated in larger amount was esterified and then afforded the enol acetate (V) ($\lambda_{max.}$ 238 mμ; log ε 4·35 in EtOH) which with monoperphthalic acid afforded an oil. This oil has a spectrum with infrared bands at 2·9 (OH), 6·0 (C:C·CO), and 5·78 μ (CO_2Me), and thus probably has structure (VI); alkaline hydrolysis and acidification affords the dihydrosantonin (VII) [infrared bands at 5·7 (γ-lactone) and 6·0 μ (C:C·CO)],

* For preliminary communications see *Chem. and Ind.*, 1955, 170; 1956, 99.

[1] Gunstone and Heggie, *J.*, 1952, 1437.
[2] McQuillin, *J.*, 1955, 528.
[3] Abe *et al.*, *J. Amer. Chem. Soc.*, 1956, **78**, 1416, 1422.

which gives the monobromo-derivative (VIII) identical with a specimen kindly provided by Dr. Abe and converted into santonin D when heated with collidine (cf. Abe *et al.*[4]).

Since epoxide rings are opened diaxially [5] in the above reaction, and since $C_{(11)}$ is attached equatorially,[3] the lactone ring in the dihydrosantonin must be *cis*-fused, in conformity with the known structure [6] of santonin D. The relatively high m. p. (135—136°) of the dihydrosantonin (VII) (cf. the isomers,[4] m. p. 87° and 115°) may be due to compact packing in the molecule, in conformity with the *cis*-fusion of the lactone ring.

Experimental.—**2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-*Octahydro*-1 : 10-*dimethyl*-2-*oxonaphthalene*** (I). 2-Methyl*cyclo*hexanone (28 g.), freshly prepared sodamide (11·2 g.), and dry ether (300 c.c.) were refluxed for 2 hr. with stirring, then evaporated to half the volume and cooled in a freezing mixture. 2-Chloroethyl ethyl ketone (31·25 g.) was added dropwise with stirring, refluxing continued for another 2 hr., and the solution then concentrated and left overnight. It was decomposed with ice-cold hydrochloric acid and extracted with ether. The extract was washed with water, dried (Na_2SO_4), and evaporated. Distillation gave unchanged 2-methyl*cyclo*hexanone, followed by the product, b. p. 110—140°/3 mm. (22·5 g.). This was refluxed with potassium hydroxide (22·5 g.) in methanol (450 c.c.) for 10 hr. in nitrogen, then neutralised with acetic acid, and the alcohol was evaporated almost completely. The residue was diluted with water and extracted twice with ether. The ethereal solution was washed with water, sodium carbonate solution, and very dilute hydrochloric acid. After removal of solvent the ketone (I) (17 g.) distilled at 110—120°/2 mm., had $\lambda_{max.}$ 247 mμ (log ε 4·1 in EtOH) and gave a 2 : 4-dinitrophenylhydrazone, m. p. 197—198° (lit., 198—199°).

Ethyl ***α-methyl-α-(1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-*octahydro*-8 : 10-*dimethyl*-7-*oxo*-2-*naphthyl*)-malonate*** (III). To a cooled solution from potassium (2·1 g.) and *tert.*-butyl alcohol (108 c.c.) was added ethyl methylmalonate (48 g.), then after 30 min. the ketone (II) (24 g.). The mixture was refluxed in nitrogen for 8 hr. and worked up in the usual way. Distillation gave a forerun of starting materials and then (by evaporative distillation) the desired diester (10·6 g.), b. p. 170—190°/0·2 mm. The product was sublimed and distilled (b. p. 180—185°/0·4 mm.; lit., 203°/1·5 mm.) (Found: C, 68·5; H, 8·5. Calc. for $C_{30}H_{36}O_6$: C, 68·5; H, 8·5%). A 2 : 4-*dinitrophenylhydrazone*, prepared therefrom in the usual way, melted at 102—104°, but repeated crystallisation from ethyl acetate yielded a small amount of red needles, m. p. 196—197° (Found: C, 65·9; H, 6·6. $C_{32}H_{36}O_6N_4$ requires C, 60·2; H, 6·5%), which was the derivative of the ethyl ester of an acid (IV).

α-(1 : 2 : 3 : 4 : 5 : 6 : 7 : 10-*Octahydro*-8 : 10-*dimethyl*-7-*oxo*-2-*naphthyl*)*propionic* acid (IV). The above keto-diester (10·5 g.) was boiled under reflux for 6 hr. with potassium hydroxide (16·8 g.), water (42 c.c.), and methanol (126 c.c.) in nitrogen. A brown oil was obtained (3 g.). This product (52 g.) from several batches was taken up in hot ethyl acetate and on recrystallisation yielded the dicarboxylic acid as needles (22·4 g.), m. p. 191—192° (lit., 204°) (Found: C, 65·0; H, 7·5. Calc. for $C_{18}H_{22}O_5$: C, 65·3; H, 7·4%).

The acid was decarboxylated at 195—200°. The brown mass was taken up in hot ethyl acetate and treated with charcoal, and the solution was concentrated and kept overnight at 0° after addition of 5—10% (by vol.) of light petroleum (b. p. 40—60°). Colourless crystals (8 g. from 22 g. of dibasic acid), m. p. 110—115°, were collected. Laborious fractional crystallisation from ethyl acetate [containing at first a few drops of light petroleum (b. p. 40—60°)] gave acids, m. p. 133—134° (lit., 135°) (1·2 g.) and 144° (lit., 145°) (0·1 g.).

The acid, m. p. 133° (2·6 g.), with diazomethane in methanol–ether gave the ester (2·5 g.) whose 2 : 4-*dinitrophenylhydrazone* formed needles (from ethyl acetate), m. p. 169—170° (Found: C, 59·2; H, 6·4. $C_{32}H_{38}O_6N_4$ requires C, 59·4; H, 6·3%). The other acid (0·2 g.) gave the *methyl ester* 2 : 4-*dinitrophenylhydrazone*, cubes (from ethyl acetate), m. p. 163—164° (Found: C, 59·2; H, 6·5%). The mixed m. p. of the two derivatives was 150—155°.

Methyl* α-(7-*acetoxy*-2 : 3 : 4 : 5 : 6 : 10-*hexahydro*-8 : 10-*dimethyl*-2-*naphthyl*)*propionate (V). The former of the above methyl esters (2 g.) was refluxed with acetic anhydride (10 c.c.) and acetyl chloride (10 c.c.) for 5 hr. in nitrogen, giving the *enol-acetate* (1·8 g.), b. p. 155°/0·2 mm. (Found: C, 70·3; H, 8·2. $C_{16}H_{24}O_4$ requires C, 70·5; H, 8·4%).

1 : 2-*Dihydrosantonin D.* To the enol acetate (1·5 g.) in ether (5 c.c.) at 0° was added 0·813*N*-ethereal monoperphthalic acid (13 c.c.), and the mixture was kept at 0° for 48 hr., most of the acid being consumed. The solution was washed with cold 10% sodium carbonate solution,

[4] Abe, Harukawa, Ishikawa, Miki, Toki, Sumi, and Toha, *Proc. Japan Acad.*, 1954, **30**, 116, 119; cf. Matsui, Toki, Kitamura, Suzuki, and Hamuro, *Bull. Chem. Soc. Japan*, 1954, **27**, 7.
[5] Turner, Anliker, Helbling, Meier, and Heusser, *Helv. Chim. Acta*, 1955, **38**, 413.
[6] Cf. *Annual Reports*, 1954, **51**, 208.

then with water, dried (Na_2SO_4), and evaporated, finally in a vacuum. The pasty residue (*ca.* 1 g.) was refluxed with potassium carbonate (0·8 g.) in methanol (40 c.c.) and water (8 c.c.) for 30 min. under nitrogen, cooled, and acidified with acetic acid (1 c.c.), and methanol was distilled off at 14 mm. Adding water (20 c.c.) gave an oil which was extracted with ether. The aqueous layer was made more acid with acetic acid (0·5 c.c.) and again extracted. The combined extracts were washed with water, dried (Na_2SO_4), and evaporated. The oil (*ca.* 0·8 g.) obtained was kept in ethyl acetate containing a few drops of light petroleum (b. p. 40—60°) at 0°. The dihydrosantonin (0·22 g.; m. p. 134°) which separated, when crystallised from ethyl acetate, had m. p. 135—136°, $\lambda_{max.}$ 245 mμ (log ε 3·9 in EtOH) (Found: C, 72·3; H, 8·2. Calc. for $C_{15}H_{20}O_3$: C, 72·5; H, 8·0%).

Santonin D (IX). To a solution of the 1 : 2-dihydrosantonin (0·5 g.) in ether (70 c.c.) was added bromine (0·24 g.) in acetic acid (2 c.c.). The monobromo-derivative slowly crystallised at 0° and formed needles, m. p. 175° (decomp.), from methanol. When mixed with an authentic sample of the bromo-derivative, m. p. 179° (decomp.), it melted at 176° (decomp.). The derivative (0·4 g.) and collidine (1·5 c.c.) were refluxed for 30 min. in nitrogen, then poured into ice-cold dilute sulphuric acid. The solid which separated was extracted with ether, washed with water, and dried (Na_2SO_4). On evaporation, crystals separated which on recrystallisation from methanol melted at 189° (lit., 190°) alone or mixed with santonin D and had $\lambda_{max.}$ 248 mμ (log ε 4·1 in EtOH) (Found: C, 72·8; H, 7·2. Calc. for $C_{15}H_{18}O_3$: C, 73·1; H, 7·3%).

Thanks are recorded to Dr. Abe for a sample of santonin D and for comparing the bromo-derivatives. Analyses were carried out by Mrs. Chhabi Dutta at the microchemical laboratory of the University College of Science, Calcutta, and infrared curves were measured by Dr. N. K. Bhattacharyya at Iowa State College. Thanks are also recorded for gifts of chemicals from the East India Pharmaceutical Works Ltd., Calcutta.

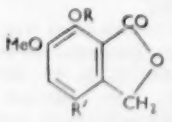
INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE,
JADAVPUR, CALCUTTA-32.

[*Received, April 24th*, 1956.]

967. *Lactones. Part IV.* A New Preparation of 7-Ethoxy-6-methoxyphthalide.*

By W. R. LOGAN and G. T. NEWBOLD.

DURING examination of the feasibility of B_{AL} phthalide fission,[1] meconin (I) was found, on reaction with ethyl sodiomalonate, ethyl sodioacetoacetate, or ethanolic sodium ethoxide to give 7-ethoxy-6-methoxyphthalide[2] (II) which has been prepared by ethylation of 7-hydroxy-6-methoxyphthalide.[2,3] The structure of the last compound has now been confirmed by infrared measurement, thus establishing rigidly that of the ether (II) (cf.



(I): R = Me, R' = H
(II): R = Et, R' = H
(III): R = Et, R' = CH_2Cl

refs. 2 and 4). Chloromethylation of the phthalide (II) gave the derivative (III) identical with that prepared[5] from 2-ethoxy-3-methoxybenzoic acid. The phthalide (II) has been characterised by conversion into 2-ethoxy-6-hydroxymethyl-3-methoxybenzhydrazide and by reduction with lithium aluminium hydride to 3-ethoxy-4-methoxyphthalyl alcohol [2-ethoxy-3 : 4-di(hydroxymethyl)-1-methoxybenzene].

Experimental.—*7-Ethoxy-6-methoxyphthalide.* (*a*) Meconin (3·0 g.) was heated under reflux with ethyl sodiomalonate in ethanol [from ethyl malonate (4·96 g., 2 mols.), sodium (0·71 g.), and ethanol (25 c.c.)] for 17 hr. The solution was concentrated under reduced pressure to 12 c.c., an equal volume of water added, and the precipitated oil (2·4 g.), which rapidly solidified, was separated. Crystallisation from aqueous ethanol gave 7-ethoxy-6-methoxyphthalide (2·0 g.)

* Part III, *J.*, 1956, 3608.

[1] Cf. Wislicenus, *Annalen*, 1886, **233**, 102.
[2] Rodionow, Kanewskaja, and Davankoff, *Ber.*, 1933, **66**, *B*, 1623.
[3] Bowman, *Ber.*, 1887, **20**, 890.
[4] Späth and Burger, *Ber.*, 1926, **59**, 1486.
[5] Manske and Ledingham, *Canad. J. Res.*, 1944, **22**, *B*, 115.

as needles, m. p. 66—67·5° (Found: C, 63·9; H, 5·9. Calc. for $C_{11}H_{12}O_4$: C, 63·45; H, 5·8%). Light absorption in EtOH: Max. at 2150 (ε 27,000) and 3090 (ε 4500); inflexion at 2400 Å (ε 7200); infrared bands in Nujol mull at 1754 (CO stretching frequency) and 1592 cm.$^{-1}$ (benzene ring). The same product (2·1 g.), m. p. and mixed m. p. 66—67°, was obtained by using ethyl acetoacetate (4·03 g.) in place of ethyl malonate. The compound was undepressed in m. p. when mixed with 7-ethoxy-6-methoxyphthalide, m. p. 65·5—66° (lit.,[3] m. p. 68—69°) obtained by ethylation of 7-hydroxy-6-methoxyphthalide which had light absorption in EtOH: Max. at 2190 (ε 23,000) and 3120 (ε 3800) and inflexion at 2350—2400 Å (ε 6500) and strong infrared bands at 1751 (in CCl_4) and 1739 cm.$^{-1}$ (in $CHCl_3$) (CO stretching frequency) consistent with the structure assigned [6] (we are indebted to Mr. J. F. Grove and Dr. L. A. Duncanson for this determination). The compound gives an indigo-blue ferric chloride colour in aqueous ethanol.

(*b*) A solution of meconin (3·0 g.) in ethanol (25 c.c.) containing sodium ethoxide from sodium (0·71 g.) was refluxed for 20 hr., then concentrated, diluted with water, and extracted with ether; removal of the ether gave a negligible residue. The aqueous phase was acidified with hydrochloric acid (Congo-red) and extracted with ether. The dried (Na_2SO_4) ethereal extract on evaporation gave an amber oil (2·95 g.) which was extracted with boiling light petroleum (b. p. 60—80°) (5 × 30 c.c.). The combined extracts were concentrated and the solid which slowly separated was repeatedly crystallised from light petroleum (b. p. 60—80°) to give 7-ethoxy-6-methoxyphthalide (1·0 g.) as needles, m. p. and mixed m. p. 66—67·5° (Found: C, 63·8; H, 6·0%). 7-Ethoxy-6-methoxyphthalide was unaffected by prolonged treatment under reflux with methanolic sodium methoxide.

4-Chloromethyl-7-ethoxy-6-methoxyphthalide. 7-Ethoxy-6-methoxyphthalide (250 mg.) was chloromethylated as described for meconin.[7] Evaporation of the chloroform extract gave a gum (0·28 g.) which rapidly solidified. A solution of the gum in benzene (25 c.c.) was passed through a column of Grade II alumina (3 × 1·5 cm.), the eluate and benzene washings (125 c.c.) were evaporated, and the residue was five times crystallised from benzene–light petroleum (b. p. 60—80°) and sublimed at 100°/10^{-3} mm., to give 4-chloromethyl-7-ethoxy-6-methoxyphthalide, m. p. 128—129·5 (lit., 130°) alone or mixed with a specimen prepared from 2-ethoxy-3-methoxybenzoic acid [8] (Found: C, 56·5; H, 5·25. Calc. for $C_{12}H_{13}O_4Cl$: C, 56·15; H, 5·1%).

2-Ethoxy-6-hydroxymethyl-3-methoxybenzhydrazide. 7-Ethoxy-6-methoxyphthalide (150 mg.) was refluxed with 90% hydrazine hydrate solution (5 c.c.) and ethanol (10 c.c.) for 4 hr. The mixture was concentrated under reduced pressure, then diluted with water, and the product isolated by using chloroform. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave the *hydrazide* (45 mg.) as needles, m. p. 149·5—150·5° (Found: C, 54·9; H, 6·6. $C_{11}H_{16}O_4N_2$ requires C, 55·0; H, 6·7%). Light absorption in EtOH: Max. at 2100 (ε 23,000) and 2840 (ε 2500), inflexions at 2325 (ε 13,000) and 3050 Å (ε 1600).

3-Ethoxy-4-methoxyphthalyl alcohol. 7-Ethoxy-6-methoxyphthalide (250 mg.) was reduced with lithium aluminium hydride as described for *m*-meconin.[8] The *diol* (120 mg.) separated from benzene–light petroleum (b. p. 40—60°) as felted needles, m. p. 64—65° depressed to 50—59° when mixed with starting material (Found: C, 62·2; H, 7·7. $C_{11}H_{14}O_4$ requires C, 62·25; H, 7·6%). Light absorption in EtOH: Max. at 2090 (ε 18,500), 2240 (ε 7800), and 2820 Å (ε 2000).

THE ROYAL TECHNICAL COLLEGE, GLASGOW. [*Received, June 12th*, 1956.]

[6] Duncanson, Grove, and Zealley, *J.*, 1953, 1331.
[7] Brown and Newbold, *J.*, 1952, 4878.
[8] Blair, Logan, and Newbold, *J.*, 1956, 3608.

---

968. *Spectra of Transition-metal Complexes of the Type* $[Co(NH_3)_5X]^{2+}$.

By J. S. GRIFFITH and L. E. ORGEL.

DATA are available on the spectra of a number of complexes of the cobaltic ion of the type $[Co(NH_3)_5X]^{2+}$, *e.g.*, where X = I, Br, Cl, or F.[1] These complexes are of the diamagnetic, spin-paired type. Here we correct and extend the results of a previous publication.[2] We discuss the spectra first on the assumption that the complexes have regular octahedral

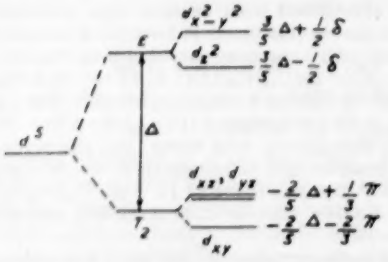
[1] Linhard and Weigel, *Z. anorg. Chem.*, 1951, **266**, 49.
[2] Orgel, *J.*, 1952, 4756.

symmetry, and then consider, as a tetragonal perturbation, the effect of the departure from it. In the former case the *d* orbitals split into two kinds, a lower t_{2g} orbital triplet and an upper e_g doublet. The ground state of the complex is represented by $(t_{2g})^6\ {}^1A_{1g}$ and the longest-wavelength spin-allowed absorptions arise from transitions to the singlets of the configuration $(t_{2g})^5(e_g)^1$. Group-theoretical arguments show that the latter singlets give rise to two triply degenerate states $^1T_{1g}$ and $^1T_{2g}$. The energies can be worked out in terms of atomic spectral parameters. In previous work one of us [3] has used Racah's parameters *A*, *B*, *C*, and the other [4] the Slater–Condon parameters F_0, F_2, F_4, so, for convenience of reference, we give the energies, relative to a suitable zero, here in terms of both :

$$\left.\begin{aligned} E[(t_{2g})^6\ {}^1A_{1g}] &= 15A - 30B + 15C = 15F_0 - 30F_2 - 60F_4 \\ E[(t_{2g})^5(e_g)^1\ {}^1T_{1g}] &= 15A - 30B + 14C + \Delta = 15F_0 - 30F_2 - 95F_4 + 10Dq \\ E[(t_{2g})^5(e_g)^1\ {}^1T_{2g}] &= 15A - 14B + 14C + \Delta = 15F_0 - 14F_2 - 175F_4 + 10Dq \end{aligned}\right\} \quad (1)$$

where $\Delta = 10Dq$ is the energy difference between the orbitals t_{2g} and e_g.

It is seen that the separation between $^1T_{1g}$ and $^1T_{2g}$ is $16B = 16F - 80F_4$ and this, therefore, should be the separation between the two longest-wavelength intense absorption bands of octahedral cobaltic complexes. Experimentally, the separation is about 8500 cm.$^{-1}$, whilst the value predicted by our theory is about twice as much. It is possible, of course, that the assignment of the bands is wrong and that the shorter-wavelength absorption band is due to a singlet from $(t_{2g})^4(e_g)^2$. Calculations indicate, however, that this is much less likely. The reason for the bad numerical agreement may be due partly to



Effect of tetragonal perturbation on the d *orbitals.*

the approximations of the theory and partly to a reduction in the values of the atomic spectral parameters in forming the complex (cf. Owen [5]).

In an earlier paper by one of us [2] the energy differences in terms of Slater–Condon parameters between the $^1T_{1g}$ and the $^1T_{2g}$ state of Co^{3+} were stated to be equal to that between the corresponding states of $^4T_{1g}$ and $^4T_{2g}$ of Cr^{3+}. The latter was given correctly as $12F_2 - 60F_4$, and is in fact only three-quarters of the separation for Co^{3+}. Also the relative order of the T_{1g} and T_{2g} levels is inverted in passing from Cr^{3+} to Co^{3+}.

We now pass on to the effect of a tetragonal distortion, to a first order in the perturbation. We suppose the ligand X to lie along the *Z* axis and have the *d* orbital splitting shown in the Figure, where $d_{x^2-y^2}$ lies above d_{z^2} because the effect of halogens on the *d* orbitals is less than that of NH_3.[6] One may expect d_{xy} to lie below (d_{xz},d_{yz}) because π interaction with the filled shells of halogens (especially for Cl, Br, or I) destabilizes the latter.

Then we write $\psi(a \longrightarrow b)$ to represent that singlet function of $(t_{2g})^5(e_g)$ in which there is one electron taken from the orbital of *a* of t_{2g} and put in the orbital *b* of e_g. The matrix of electrostatic energy is then

$$M = (15A + 14C)I - 2KB = (15F_0 - 245F_4)I - 2K(F_2 - 5F_4) \quad . \quad . \quad (2)$$

[3] Griffiths, *J. Inorg. Nucl. Chem.*, 1956, **2**, 1, 229.
[4] Orgel, *J. Chem. Phys.*, 1955, **23**, 1819.
[5] Owen, *Proc. Roy. Soc.*, 1955, *A*, **227**, 183.
[6] Orgel, *J. Chem. Phys.*, 1955, **23**, 1004.

where I is the unit matrix and

$K =$

	$\psi(d_{yz} \rightarrow d_{z^2})$	$\psi(d_{zx} \rightarrow d_{z^2})$	$\psi(d_{xy} \rightarrow d_{z^2})$	$\psi(d_{yz} \rightarrow d_{x^2-y^2})$	$\psi(d_{zx} \rightarrow d_{x^2-y^2})$	$\psi(d_{xy} \rightarrow d_{x^2-y^2})$
$\psi(d_{yz} \rightarrow d_{z^2})$	13	0	0	$2\sqrt{3}$	0	0
$\psi(d_{zx} \rightarrow d_{z^2})$	0	13	0	0	$2\sqrt{3}$	0
$\psi(d_{xy} \rightarrow d_{z^2})$	0	0	7	0	0	0
$\psi(d_{yz} \rightarrow d_{x^2-y^2})$	$2\sqrt{3}$	0	0	9	0	0
$\psi(d_{zx} \rightarrow d_{x^2-y^2})$	0	$2\sqrt{3}$	0	0	9	0
$\psi(d_{xy} \rightarrow d_{x^2-y^2})$	0	0	0	0	0	15

. . . . . (3)

From (2) the zero-order wave-functions are easily seen to be

$$\left.\begin{array}{c} \frac{1}{2}\sqrt{3}\psi(d_{yz} \longrightarrow d_{z^2}) + \frac{1}{2}\psi(d_{yz} \longrightarrow d_{x^2-y^2}) \\ \frac{1}{2}\sqrt{3}\psi(d_{zx} \longrightarrow d_{z^2}) + \frac{1}{2}\psi(d_{zx} \longrightarrow d_{x^2-y^2}) \\ \psi(d_{xy} \longrightarrow d_{x^2-y^2}) \end{array}\right\} \in {}^1T_{1g} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and

$$\left.\begin{array}{c} -\frac{1}{2}\psi(d_{yz} \longrightarrow d_{z^2}) + \frac{1}{2}\sqrt{3}\psi(d_{yz} \longrightarrow d_{x^2-y^2}) \\ -\frac{1}{2}\psi(d_{zx} \longrightarrow d_{z^2}) + \frac{1}{2}\sqrt{3}\psi(d_{zx} \longrightarrow d_{x^2-y^2}) \\ (d_{xy} \longrightarrow d_{z^2}) \end{array}\right\} \in {}^1T_{2g} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Application of the tetragonal perturbation to these functions now gives $(\frac{3}{4}\delta + \pi)$ and $(\frac{3}{4}\delta - \pi)$ as the respective splittings of the two levels ${}^1T_{1g}$ and ${}^1T_{2g}$. In a previous paper [2] it was incorrectly stated that the upper excited state is not split to a first order in perturbation. If, however, our choice of positive signs for δ and π are correct, it is still true that the lower excited state is split more than the upper one. Furthermore, for the lower excited states the doublet should indeed be lower than the singlet in accord with the intensity measurements of Linhard and Weigel.[1] Provided that $\frac{3}{4}\delta > \pi$, the reverse is true for the upper states.

UNIVERSITY CHEMICAL LABORATORY,
PEMBROKE STREET, CAMBRIDGE.

[*Received, June 25th*, 1956.]

---

969. *2-Acyl Derivatives of Cyclic 1 : 3-Diones. Part IV.* The Structure of Dehydroleptospermone.*

By W. R. CHAN and C. H. HASSALL.

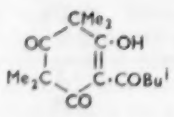
IT has been shown [1] that pyrolysis of the crude product of bromination of leptospermone (I) leads to dehydroleptospermone, $C_{15}H_{20}O_4$. The same compound may be prepared by dehydrobromination of monobromoleptospermone with collidine or with fused potassium acetate in methanol. Some interest attaches to the structure of dehydroleptospermone in view of early proposals, which have, however, been refuted recently,[2] that natural products such as flavaspidic acid [3] and protokosin [4] contain dehydro-2-acyl*cyclo*hexane-1 : 3-dione units in their molecular constitution.

Dehydroleptospermone does not behave like a 2-acyl*cyclo*hexane-1 : 3-dione. It is insoluble in alkali carbonates, does not form a chloroform-soluble copper derivative, and gives no colour with ferric chloride solution. The ultraviolet absorption spectrum has maxima at 231 (ε 11,000) and 260 mμ (ε 11,800) while 2-acyl*cyclo*hexane-1 : 3-diones regularly [5] have maxima near 230 and 280 mμ. Acetylation of dehydroleptospermone

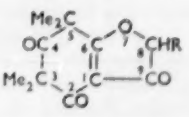
* Part III, Chan and Hassall, *J.*, 1956, 3495.

[1] Briggs, Hassall, and Short, *J.*, 1945, 706.
[2] Birch, *J.*, 1951, 3026; Birch and Todd, *J.*, 1952, 3102.
[3] Boehm, *Annalen*, 1903, **320**, 310.
[4] Hems and Todd, *J.*, 1937, 562.
[5] Chan and Hassall, *J.*, 1956, 3495.

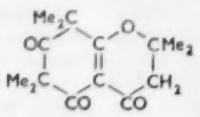
gives a monoacetate with a single ultraviolet absorption maximum at 267 mμ (ε 6100). A comparison of the infrared absorption spectrum of this compound with that of dehydroleptospermone suggests that it is an enol acetate. This evidence indicates that dehydroleptospermone may have the constitution (II) or (IV). To distinguish these possibilities



(I)



(II) : R = Pr^i
(III) : R = H



(IV)

the dehydrobromination of the monobromo-derivative of 6-acetyl-2 : 2 : 4 : 4-tetramethyl-*cyclo*hexane-1 : 3 : 5-trione has been studied. The product of the reaction, which i formulated as 3 : 3 : 5 : 5-tetramethyl-7-oxa*bicyclo*[4 : 3 : 0]non-1(6)ene-2 : 4 : 9-trione (III), has properties very similar to those of dehydroleptospermone. The ultraviolet absorption spectra of the two compounds have similar maxima. The infrared absorption spectra have corresponding maxima in the carbonyl and double-bond region 1800–1450 cm.$^{-1}$, and are in agreement with the constitutions (II) and (III) which are proposed. The close similarity of absorption spectra would not be expected if the dehydro-derivatives of leptospermone and 6-acetyl-2 : 2 : 4 : 4-tetramethyl*cyclo*hexane-1 : 3 : 5-trione have the structures (IV) and (III) respectively. This indicates that dehydroleptospermone should be assigned the constitution (II).

Experimental.—Light petroleum refers to the fraction of b. p. 60—80°.

Ultraviolet spectra were determined for methanol solutions with a Beckman spectrophotometer, model DU.

Dehydroleptospermone (3 : 3 : 5 : 5-*tetramethyl*-8-iso*propyl*-7-*oxa*bicyclo[4 : 3 : 0]*non*-1(6)-*ene*-2 : 4 : 9-*trione*). A solution of leptospermone (5·0 g.) and bromine (3·5 g.) in chloroform (5 c.c.) was set aside for 5 days. Bromine and solvent were then removed *in vacuo*. The oily residue did not crystallise. Attempts to distil it at 0·3 mm. led to decomposition. The active bromine in this residue was estimated by using potassium iodide and sodium thiosulphate (Found : Br, 25·7. Calc. for $C_{15}H_{21}O_4Br$: Br, 23·2%).

When the residue was heated at atmospheric pressure for 4 hr. at 130—140° there was considerable evolution of hydrogen bromide, and a solid was obtained. This was recrystallised from ethyl acetate and light petroleum to give a poor yield of dehydroleptospermone, white needles, m. p. 125—130° [Found : C, 68·4; H, 7·7%; *M* (cryoscopic in camphor), 248. Calc. for $C_{15}H_{20}O_4$: C, 68·2; H, 7·6%; *M*, 264]. It gave no colour with tetranitromethane or ferric chloride. A higher yield was obtained when the residue from the bromination reaction was refluxed with γ-collidine (15 c.c.) for 1½ hr. The solid obtained by pouring the mixture into excess of dilute hydrochloric acid was collected after 12 hr., washed successively with 3N-hydrochloric acid (100 c.c.), 10% sodium carbonate solution (100 c.c.), and water (300 c.c.), then chromatographed on acid-washed alumina. The material eluted with benzene (3·7 g.; m. p. 110—114°) was recrystallised repeatedly from light petroleum, to yield white needles, identical with the previous product by m. p., mixed m. p., and ultraviolet absorption.

Alternatively, the residue from the bromination (310 mg.), fused potassium acetate (135 mg.), and methanol (10 c.c.) were refluxed for 2 hr. Water (25 c.c.) was added to the residue after removal of the methanol, and the mixture acidified with hydrochloric acid to give a white solid (167 mg.) affording dehydroleptospermone on recrystallisation from light petroleum. The *acetate* was obtained by refluxing dehydroleptospermone (102 mg.) with 5 c.c. of acetic anhydride–acetyl chloride (4 : 1 v/v) for 2½ hr. It recrystallised from light petroleum as large cubes, m. p. 94—95° (Found : C, 67·4; H, 7·3; Ac, 16·6. $C_{17}H_{22}O_5$ requires C, 66·7; H, 7·2; 1Ac, 14·1%), $\lambda_{max.}$ 267 mμ (ε 6100). It gave a yellow colour with tetranitromethane.

6-*Acetyl*-2 : 2 : 4 : 4-*tetramethyl*cyclo*hexane*-1 : 3 : 5-*trione*. This compound was prepared according to the directions of Riedl and Risse.[6] It was obtained from the fraction soluble in potassium hydrogen carbonate, by steam-distillation, as long needles, m. p. 35·5—36°, $\lambda_{max.}$ 234 and 277 mμ (ε 8500 and 10,500 respectively). The *piperonylidene derivative* recrystallised from

[6] Riedl and Risse, *Annalen*, 1954, **585**, 209.

methanol as yellow plates, m. p. 153—154° (Found: C, 67·6; H, 5·6. $C_{20}H_{20}O_4$ requires C, 67·4; H, 5·7%).

3 : 3 : 5 : 5-*Tetramethyl*-7-*oxa*bicyclo[4 : 3 : 0]*non*-1(6)-*ene*-2 : 4 : 9-*trione* (III). The triketone (615 mg.) and bromine (397 mg.) in chloroform (3 c.c.) were kept for 20 hr. at room temperature. After removal of the solvent, the oily product (832 mg.) was mixed with dry methanol (20 c.c.) and fused potassium acetate (410 mg.). After 1 hour's refluxing on a water-bath the methanol was distilled off and water (100 c.c.) added. The aqueous solution was extracted with ether (4 × 50 c.c.). The semi-liquid residue obtained after evaporation of ether from the combined extracts was triturated with ether (2 × 3 c.c.), to give a relatively insoluble *product* which recrystallised from methanol as white needles (166 mg.), m. p. 173—175° [Found: C, 65·4; H, 6·3; *M* (Rast), 228. $C_{13}H_{14}O_4$ requires C, 64·9; H, 6·35%; *M*, 222]. $\lambda_{max.}$ 232 and 260 mμ (ε 10,000 and 11,400 respectively). The compound gave no colour with tetranitromethane. The *acetate*, prepared as described for dehydroleptospermone, crystallised as needles (from light petroleum), m. p. 100—101° (Found: C, 63·6; H, 6·1; Ac, 16·9. $C_{14}H_{14}O_5$ requires C, 63·6; H, 6·1; 1Ac, 16·3%). $\lambda_{max.}$ 263 mμ (ε 6000). It gave a yellow colour with tetranitromethane.

Infrared absorption spectra. The infrared spectra were determined in potassium bromide pellets by Dr. S. M. Nagy, Massachusetts Institute of Technology, using a Baird Associates instrument. The principal bands observed between 4000 and 1400 cm.$^{-1}$ were as follows (s = strong, m = medium, w = weak, sh = shoulder):

Dehydroleptospermone: 3310 w, 3150 w, 2900 m, 2860 m, 1724 s, 1695 s, 1650 m, 1587 s, 1473 s, 1425 s.

Compound (III): 3310 m, 2900 m, 2860 m, 1724 s, 1695 s, 1645 s, 1587 s, 1470 s, 1425 s, 1404 m.

Dehydroleptospermone acetate: 3310 w, 2900 m, 1754 m, 1709 m, 1667 s, 1592 m, 1462 m, 1450 sh.

Enol acetate of (III): 3310 w, 2874 m, 1739 s, 1700 m, 1660 s, 1603 m, 1550 w, 1470 m, 1450 m.

One of us (W. R. C.) acknowledges with thanks the award of a Geddes Grant Research Fellowship and a grant from Messrs. Roche Products Ltd.

UNIVERSITY COLLEGE OF THE WEST INDIES,
JAMAICA, B.W.I.

[*Received, July 4th*, 1956.]

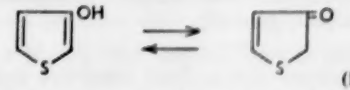
---

970. 3-*Hydroxythiophen.*

By M. C. FORD and DONALD MACKAY.

UNTIL recently neither of the monohydroxythiophens was known. 2-Hydroxythiophen, however, has been obtained [2] pure (cf. Mentzer and Billet [1]), but in low yield, from the mixture of magnesium complexes formed by the action of oxygen, at 0—5°, on ethereal 2-thienylmagnesium bromide in the presence of *iso*propylmagnesium bromide. It was a low-melting solid with a non-phenolic odour; two non-phenolic tautomers, 2 : 3-dihydro- and 2 : 5-dihydro-2-oxothiophen, are possible, indeed the infrared spectrum of a carbon tetrachloride solution exhibited a strong carbonyl band but only weak hydroxyl absorption, and, in addition to *O*-acyl derivatives, a benzylidene derivative could be prepared.

The similar oxidation of 3-thienylmagnesium bromide was stated to yield a crude material that could not be purified, though qualitative tests showed it to contain phenolic material. Other possible routes to 3-hydroxythiophen (I) do not seem to have been explored.

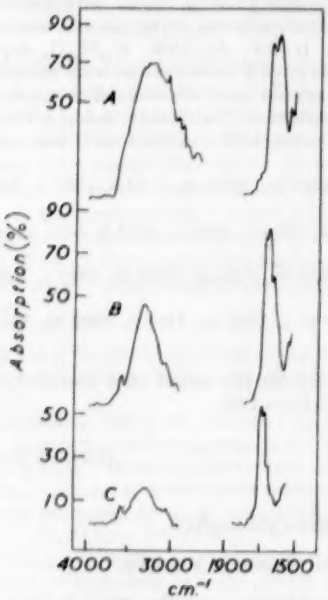


(I) (II)

As an authentic specimen was needed the Grignard method was re-examined: the production of a crude phenolic material was confirmed, and two distillations gave the pure hydroxythiophen, which was, however, unstable, developing a reddish tinge and a disagreeable odour within a day, and finally resinifying.

[1] Mentzer and Billet, *Bull. Soc. chim. France*, 1945, 292.
[2] Hurd and Kreuz, *J. Amer. Chem. Soc.*, 1950, **72**, 5543.

The spectrum of a liquid film (*A*) in the range 4000—1500 cm.$^{-1}$ exhibits a broad band centred at 3300 cm.$^{-1}$ characteristic of a hydrogen-bonded phenolic hydroxyl group, whilst the triple peak (1665, 1644, and 1630 cm.$^{-1}$), which is of a very similar intensity, shows the presence of the αβ-unsaturated carbonyl system; hydrogen-bonding of the carbonyl group may perhaps account for the complexity of the band. In the spectra (*B* and *C*) of increasingly dilute carbon tetrachloride solutions the shoulder originally present at 3585 cm.$^{-1}$ emerges as a separate peak at 3600 cm.$^{-1}$, indicating a progressive increase in the proportion of free hydroxyl group. There is a marked accompanying increase in the relative intensity of the unsaturated carbonyl band, together with a displacement of its maximum towards higher frequencies (see Figure).



Tautomerism of 3-hydroxythiophen: hydroxyl and carbonyl bands.
A, liquid film.
B, 15% v./v. in CCl_4.
C, 8% v./v. in CCl_4.

The absorption characteristic of an unsaturated carbonyl group clearly establishes the presence of the tautomeric 2 : 3-dihydro-3-oxothiophen (II) in the liquid and in solutions. The changes in the relative intensities of the carbonyl and hydroxyl bands suggest a shifting of equilibrium in favour of the oxo-form with increasing dilution, though a difference between the transition moments for the free and the hydrogen-bonded carbonyl group could also be responsible for this effect. However, the strength of the hydroxyl band in the spectrum of the liquid film, and the odour, suggest that the pure substance must be phenolic to a comparable extent.

There is thus a marked contrast between 2-hydroxythiophen which probably exists, not unexpectedly, largely in a ketonic form (indeed the crystalline solid may be in reality 2 : 5-dihydro-2-oxothiophen) and 3-hydroxythiophen which, though also tautomeric, is nevertheless noticeably phenolic.

Experimental.—A solution of ethyl bromide (18·5 g.) and 3-bromothiophen [3] (b. p. 157—158·5°/759 mm.; 37·0 g.) in ether (150 ml.) was added to a briskly reacting mixture of ethyl bromide (18·5 g.), magnesium (13·7 g.), and ether (200 ml.) in such a way that the vigour of the original reaction was maintained; the whole was then refluxed for 18 hr. in nitrogen. A solution of *iso*propylmagnesium bromide [from *iso*propyl bromide (35·0 g.), magnesium (7·0 g.), and ether (100 ml.)] was added, the mixture was cooled to −10°, and dry oxygen was passed, the temperature being maintained below 5°. When absorption of the gas had ceased the product was set aside at 5° for 20 hr. and then poured on powdered solid carbon dioxide. After

[3] Hartough, "Thiophene and its Derivatives," Interscience, New York, 1952, p. 499.

addition of a slight excess of chilled 2N-sulphuric acid the ether layer was separated, and the aqueous layer saturated with salt and further extracted. The ethereal solutions were combined and, after a preliminary washing with 2N-potassium hydrogen carbonate, extracted with 5N-sodium hydroxide. The alkaline solution was immediately acidified with ice-cold 2N-sulphuric acid and the liberated phenolic material then taken up in ether.

Removal of the solvent under reduced pressure from the dried ($MgSO_4$) solution gave an almost black product (2·2 g.) which was first stored (5°/400 mm.) over phosphoric oxide and then distilled from glass wool: a pale yellow liquid, b. p. 38—39°/0·01 mm., was obtained, which when redistilled under nitrogen at 0·02 mm. (bath ≯ 80°) yielded the unstable *3-hydroxythiophen* 5%) as an almost colourless, slightly viscous, oil with a phenolic odour (Found: C, 47·1; H, 4·3. C_4H_4OS requires C, 48·0; H, 4·0%). The analytical and infrared results were obtained within 2 hr. of the final distillation, during which time the deterioration of a reference sample was almost imperceptible.

With aqueous ferric chloride the hydroxythiophen gave an intensely red colour, and with diazotised aniline in presence of alkali, a dark red precipitate.

The *benzoate*, prepared under Schotten–Baumann conditions, was obtained as irregular prisms, m. p. 40°, from light petroleum (b. p. 30—40°) (Found: C, 64·7; H, 4·2; S, 15·4. $C_{11}H_8O_2S$ requires C, 64·7; H, 3·95; S, 15·7%): its m. p. was strongly depressed by admixture with the isomeric 2-thienyl benzoate,[3] m. p. 44°, a liquid being formed at room temperature; the 3 : 5-*dinitrobenzoate*, prepared in pyridine solution and recrystallised from methanol, formed minute, faintly yellow, prisms, m. p. 150° (Found: C, 45·1; H, 2·3. $C_{11}H_6O_6N_2S$ requires C, 44·9; H, 2·1%). The *phenylcarbamate* was prepared in the absence of a solvent and in the cold, a trace of pyridine being used as catalyst; recrystallised from light petroleum (b. p. 70—80°) it gave felted needles, m. p. 120° (Found: C, 60·3; H, 4·4; N, 6·1. $C_{11}H_9O_2NS$ requires C, 60·25; H, 4·1; N, 6·4%). The derivatives all appeared to be stable indefinitely.

3-Bromothiophen (20 g.) was recovered from the ethereal solution of alkali-insoluble material.

Grateful acknowledgment is made to Dr. D. C. McKean with whom the infrared results were discussed. One of us (D. M.) also thanks the Carnegie Trust for the Universities of Scotland for a scholarship, and the Murdo Macaulay Trust for a grant.

THE UNIVERSITY, OLD ABERDEEN. [*Received, July 12th,* 1956.]

---

971. *The Fission of Alkyl Allyl Ethers by Boron Trichloride.*

By W. GERRARD, M. F. LAPPERT, and H. B. SILVER.

EXPERIMENTS with boron trichloride and mixed dialkyl or alkyl aryl ethers have indicated that, in general, ether fission occurs readily and that the nature of the products depends on the proportions in which the reagents are mixed [see schemes (1) and (2)].

$$(1)\quad ROR' + BCl_3 \longrightarrow RO{\cdot}BCl_2 + R'Cl$$

$$(2)\quad 2ROR' + BCl_3 \longrightarrow (RO)_2B{\cdot}Cl + 2R'Cl$$

Moreover, it has been shown that the alkyl chloride is produced exclusively from the more electron-releasing (R′) of the two groups and that the mechanism of the fission is of the S_N1 type.[1]

We have described the fission of diallyl, di-2-methylallyl, and allyl 2-methylallyl ethers [2] and now report results obtained with allyl butyl (*n-*, *sec.-*, and *tert.-*) and allyl propyl (*n-* and *iso-*) ethers. The purpose of the investigation was partly that the results are of interest *per se*, but also to determine the degree of electron-release of the allyl group relative to these saturated alkyl groups. We believe that the fission of mixed ethers by boron trichloride provides a general method of determining relative electron-release of hydrocarbon radicals.

Reaction (2) was employed except in the allyl *n*-butyl ether system, because dichloroboronites, $RO{\cdot}BCl_2$, particularly those wherein R = a *sec.-* or *tert.*-alkyl or an allyl group,

[1] Gerrard and Lappert, *J.*, 1951, 1020; 1952, 1486; Edwards, Gerrard, and Lappert, *J.*, in the press.

are unstable.[2,3] Whilst the corresponding chloroboronates, $(RO)_2B{\cdot}Cl$, are likewise unstable,[2,4] their manner of decomposition is known [see scheme (3)], and therefore permits the fate of the group R to be traced by isolation and identification of the borate, $B(OR)_3$.

$$(3)\quad 3(RO)_2B{\cdot}Cl \longrightarrow 3RCl + B_2O_3 + B(OR)_3$$

The experiments show that the primary alkyl allyl ethers give allyl chloride and the primary alkoxyboron chloride, whereas the *sec.*- or *tert.*-alkyl allyl ethers produce the reverse mode of fission. We conclude, therefore, that the electron-releasing power of the allyl group is intermediate between that of primary and secondary alkyl groups. This view is supported by Vernon's measurements of first-order rate coefficients for the solvolysis of allyl and *n*-propyl chloride.[5] Our earlier experiments on allylic systems had also indicated that the reactivity of the allyl group is greater than that of a primary alkyl group.

Experimental.—General procedures have been described before.[3] The allyl propyl ethers were prepared by a Williamson synthesis from the appropriate sodium propoxide and allyl bromide. The allyl butyl ethers were obtained by the method of Talley, Hunter, and Yanovsky.[6]

Allyl n-*butyl ether.* The ether (4·98 g., 1 mol.) in *n*-pentane (10 c.c.) was added (20 min.) to boron trichloride (5·67 g., 1·1 mol.) in *n*-pentane (10 c.c.) at −80°. An orange-red lower layer separated, but at 20° the mixture was homogeneous. After 2 hr. at 20°/15 mm., *n*-butyl dichloroboronite (5·81 g., 90%) remained as a pale brown, liquid residue, having b. p. 29°/9 mm., n_D^{21} 1·4158 (Found: Cl, 45·2; B, 7·0. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%).

Allyl sec.-*butyl ether.* The ether (11·50 g., 2 mols.) in *n*-pentane (15 c.c.) was added (20 min.) to the trichloride (5·90 g., 1 mol.) in *n*-pentane at −80°, whereupon a yellow lower layer separated. Matter volatile at 20°/15 mm. was removed by suction (1 hr.). A non-volatile residue (7·47 g.) remained. This was heated (1 hr.) at 140° under reflux, the outlet of the condenser being connected to a cold (−80°) trap. A condensate of crude allyl chloride (2·05 g.), b. p. 42—46°/760 mm., n_D^{20} 1·4105, was collected, leaving a residue (4·98 g.), which afforded triallyl borate (2·95 g., 91%), b. p. 72°/10 mm., n_D^{20} 1·4285 (Found: B, 6·0. Calc. for $C_9H_{15}O_3B$: B, 5·95%), and a residue of boron trioxide (1·075 g., 93%) on distillation.

Allyl tert.-*butyl ether.* The ether (6·91 g., 2 mols.) was slowly added to the trichloride (3·55 g., 1 mol.) at −80°, in the absence of solvent. A pale orange solution was formed. Evacuation at 20°/18 mm. yielded crude *tert.*-butyl chloride (3·56 g., 64%), b. p. 50°/730 mm., n_D^{20} 1·3805 [Found: Cl (all hydrolysable in the cold, characteristic of *tert.*-butyl, but not allyl chloride), 36·8. Calc. for C_4H_9Cl: Cl, 38·4%]. The residue (6·70 g.), after being heated (3 hr.) under reflux at 110°, afforded a condensate (2·93 g.), collected at −80°, which was a mixture of *tert.*-butyl and allyl chloride, b. p. 46—48°/760 mm., n_D^{20} 1·4025 (Found: easily hydrolysable Cl, 21·3; total Cl, 42·0%), and triallyl borate (1·45 g., 79%), b. p. 70°/12 mm. (Found: B, 5·8%).

Allyl n-*propyl ether.* The ether (5·94 g., 2 mols.) in *n*-pentane (10 c.c.) was added dropwise (20 min.) to the trichloride (3·48 g., 1 mol.) in *n*-pentane (5 c.c.) at −80°. A yellow lower layer separated; at 20° the mixture appeared homogeneous and was a deep orange colour. Evacuation at 20°/15 mm. afforded a liquid condensate (5·04 g.), which on distillation gave di-*n*-propyl chloroboronate (4·10 g., 84%), b. p. 38·5°/6 mm., n_D^{20} 1·4036 (Found: Cl, 22·0; B, 6·7. Calc. for $C_6H_{14}O_2ClB$: Cl, 22·0; B, 6·7%).

Allyl iso*propyl ether.* The ether (7·51 g., 2 mols.) was added to the trichloride (4·40 g., 1 mol.) in *n*-pentane (15 c.c.) at −80°. A white solid was formed, but disappeared when the addition had been completed. To the mixture at −80° was added ferric chloride (0·05 g.), to facilitate decomposition of the chloroboronate,[4] and the product was warmed to 20°. Matter volatile at 20°/18 mm. was removed by suction and the residue (3·16 g.) was distilled, to afford triallyl borate (1·67 g., 74%), b. p. 66°/13 mm., n_D^{20} 1·4267 (Found: B, 6·0%), and a residue containing boron trioxide (0·871 g., 100%).

THE NORTHERN POLYTECHNIC,
HOLLOWAY ROAD, LONDON, N.7.

[*Received, July 19th, 1956.*]

[2] Gerrard, Lappert, and Silver, *J.*, 1956, 3285.
[3] Gerrard and Lappert, *J.*, 1951, 2545; 1955, 3084.
[4] Lappert, *J.*, 1956, 1768.
[5] Vernon, *J.*, 1954, 423.
[6] Talley, Hunter, and Yanovsky, *J. Amer. Chem. Soc.*, 1951, **73**, 3528.

THE INDEX TO THIS VOLUME HAS BEEN REMOVED FROM THIS POSITION AND PLACED AT THE BEGINNING OF THE FILM FOR THE CONVENIENCE OF READERS

are unstable.[2,3] Whilst the corresponding chloroboronates, $(RO)_2B{\cdot}Cl$, are likewise unstable,[2,4] their manner of decomposition is known [see scheme (3)], and therefore permits the fate of the group R to be traced by isolation and identification of the borate, $B(OR)_3$.

$$(3)\quad 3(RO)_2B{\cdot}Cl \longrightarrow 3RCl + B_2O_3 + B(OR)_3$$

The experiments show that the primary alkyl allyl ethers give allyl chloride and the primary alkoxyboron chloride, whereas the *sec.*- or *tert.*-alkyl allyl ethers produce the reverse mode of fission. We conclude, therefore, that the electron-releasing power of the allyl group is intermediate between that of primary and secondary alkyl groups. This view is supported by Vernon's measurements of first-order rate coefficients for the solvolysis of allyl and *n*-propyl chloride.[5] Our earlier experiments on allylic systems had also indicated that the reactivity of the allyl group is greater than that of a primary alkyl group.

Experimental.—General procedures have been described before.[2] The allyl propyl ethers were prepared by a Williamson synthesis from the appropriate sodium propoxide and allyl bromide. The allyl butyl ethers were obtained by the method of Talley, Hunter, and Yanovsky.[6]

Allyl n-*butyl ether.* The ether (4·98 g., 1 mol.) in *n*-pentane (10 c.c.) was added (20 min.) to boron trichloride (5·67 g., 1·1 mol.) in *n*-pentane (10 c.c.) at −80°. An orange-red lower layer separated, but at 20° the mixture was homogeneous. After 2 hr. at 20°/15 mm., *n*-butyl dichloroboronite (5·81 g., 90%) remained as a pale brown, liquid residue, having b. p. 29°/9 mm., n_D^{21} 1·4158 (Found: Cl, 45·2; B, 7·0. Calc. for $C_4H_9OCl_2B$: Cl, 45·8; B, 7·0%).

Allyl sec.-*butyl ether.* The ether (11·50 g., 2 mols.) in *n*-pentane (15 c.c.) was added (20 min.) to the trichloride (5·90 g., 1 mol.) in *n*-pentane at −80°, whereupon a yellow lower layer separated. Matter volatile at 20°/15 mm. was removed by suction (1 hr.). A non-volatile residue (7·47 g.) remained. This was heated (1 hr.) at 140° under reflux, the outlet of the condenser being connected to a cold (−80°) trap. A condensate of crude allyl chloride (2·05 g.), b. p. 42—46°/760 mm., n_D^{20} 1·4105, was collected, leaving a residue (4·98 g.), which afforded triallyl borate (2·95 g., 91%), b. p. 72°/10 mm., n_D^{20} 1·4285 (Found: B, 6·0. Calc. for $C_9H_{15}O_3B$: B, 5·95%), and a residue of boron trioxide (1·075 g., 93%) on distillation.

Allyl tert.-*butyl ether.* The ether (6·91 g., 2 mols.) was slowly added to the trichloride (3·55 g., 1 mol.) at −80°, in the absence of solvent. A pale orange solution was formed. Evacuation at 20°/18 mm. yielded crude *tert.*-butyl chloride (3·56 g., 64%), b. p. 50°/730 mm., n_D^{20} 1·3805 [Found: Cl (all hydrolysable in the cold, characteristic of *tert.*-butyl, but not allyl chloride), 36·8. Calc. for C_4H_9Cl: Cl, 38·4%]. The residue (6·70 g.), after being heated (3 hr.) under reflux at 110°, afforded a condensate (2·93 g.), collected at −80°, which was a mixture of *tert.*-butyl and allyl chloride, b. p. 46—48°/760 mm., n_D^{20} 1·4025 (Found: easily hydrolysable Cl, 21·3; total Cl, 42·0%), and triallyl borate (1·45 g., 79%), b. p. 70°/12 mm. (Found: B, 5·8%).

Allyl n-*propyl ether.* The ether (5·94 g., 2 mols.) in *n*-pentane (10 c.c.) was added dropwise (20 min.) to the trichloride (3·48 g., 1 mol.) in *n*-pentane (5 c.c.) at −80°. A yellow lower layer separated; at 20° the mixture appeared homogeneous and was a deep orange colour. Evacuation at 20°/15 mm. afforded a liquid condensate (5·04 g.), which on distillation gave di-*n*-propyl chloroboronate (4·10 g., 84%), b. p. 38·5°/6 mm., n_D^{20} 1·4036 (Found: Cl, 22·0; B, 6·7. Calc. for $C_6H_{14}O_2ClB$: Cl, 22·0; B, 6·7%).

Allyl iso*propyl ether.* The ether (7·51 g., 2 mols.) was added to the trichloride (4·40 g., 1 mol.) in *n*-pentane (15 c.c.) at −80°. A white solid was formed, but disappeared when the addition had been completed. To the mixture at −80° was added ferric chloride (0·05 g.), to facilitate decomposition of the chloroboronate,[4] and the product was warmed to 20°. Matter volatile at 20°/18 mm. was removed by suction and the residue (3·16 g.) was distilled, to afford triallyl borate (1·67 g., 74%), b. p. 66°/13 mm., n_D^{20} 1·4267 (Found: B, 6·0%), and a residue containing boron trioxide (0·871 g., 100%).

THE NORTHERN POLYTECHNIC,
HOLLOWAY ROAD, LONDON, N.7.

[*Received, July 19th,* 1956.]

[2] Gerrard, Lappert, and Silver, *J.*, 1956, 3285.
[3] Gerrard and Lappert, *J.*, 1951, 2545; 1955, 3084.
[4] Lappert, *J.*, 1956, 1768.
[5] Vernon, *J.*, 1954, 423.
[6] Talley, Hunter, and Yanovsky, *J. Amer. Chem. Soc.*, 1951, **73**, 3528.

THE CHEMICAL SOCIETY

'SPECIAL PUBLICATION' NO. 4

RECENT ADVANCES IN THE CHEMISTRY OF COLOURING MATTERS

This report of a Symposium held in London on 2nd February, 1956, is the fourth in The Chemical Society's series of Special Publications. The following are the main contributions:

"Steric Effects in Azo and Indigo Dyes," by Wallace R. Brode (Washington).
"*cis-trans*-Isomerism in Azo-dyes," by E. Atherton and R. H. Peters.
"Synthesis of Azaporphins and Related Macrocycles," by J. A. Elvidge (Imperial College).
"Synthetic Carotenoids," by O. Isler, H. Lindlar, M. Montavon, R. Rüegg, G. Saucy, and P. Zeller (Basle).
"Modern Theories of Colour," by M. J. S. Dewar (London).

In addition to the above papers, much information is given in the report of the discussion, which is included in the publication.

Price: 15s.

THE CHEMICAL SOCIETY, BURLINGTON HOUSE, LONDON W.1.

CURRENT CHEMICAL PAPERS

Current Chemical Papers is a monthly classified world list of new papers in pure chemistry. Each issue normally contains the titles of relevant papers contained in all journals received during the whole of the previous month. In addition to the normal issue it can be obtained printed on one side of the paper only, for the benefit of those wishing to use the publication for the compilation of their own card index system. It is also available for countries outside Europe as an Air Mail Edition.

The attention of subscribers in the U.S.A. and Canada is directed particularly to the Air Mail Edition. This edition will frequently contain titles of papers published in European journals before the journals are available in North America.

WRITE FOR A FREE SPECIMEN COPY

Price per annum, including postage:

Ordinary Edition	£3 10s. 0d.
Edition printed on one side of the paper	£5 0s. 0d.
Air Mail Edition (for countries outside Europe)	£6 0s. 0d.

THE CHEMICAL SOCIETY, BURLINGTON HOUSE, LONDON W.1.

LABORATORY BDH CHEMICALS

***N*-Methyl-*N*-nitroso-toluene-*p*-sulphonamide**

$CH_3.C_6H_4.SO_2.N(CH_3).NO$

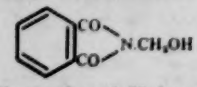
Diazomethane, well known as a valuable and versatile reagent, can be generated easily and safely in solution in ether or in ether and alcohol by treating *N*-methyl-*N*-nitroso-toluene-*p*-sulphonamide with potassium hydroxide in a suitable medium (de Boer and Backer, *Proc. Koninkl. Ned. Akad. Wetenschap.*, 1952, **55B**, 444; *Rec. trav. chim.*, 1954, **73**, 229).

The sulphonamide is issued in very pale yellow crystals, melting point 58-60° C.

10 g 6/6 25 g 13/- 100 g 44/6

Packages extra, returnable

***N*-Hydroxy-methyl-phthalimide**



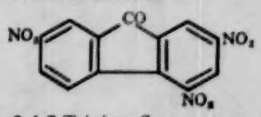
Winstead and Heine (*J. Amer. Chem. Soc.*, 1955, **77**, 1913) have shown that *N*-hydroxy-methyl-phthalimide is a valuable reagent for the identification of amines. The amine to be identified is refluxed with a 10% solution of hydroxy-methyl-phthalimide in 80% ethanol for ½-2 hours and the *N*-arylamino-methyl-phthalimide separates as a crystalline product on cooling. The thirty derivatives prepared by Winstead and Heine melt in the range 112° C to 242° C.

N-Hydroxy-methyl-phthalimide is supplied as an off-white, crystalline powder, melting point 142-144° C.

5 g 3/9 10 g 6/9 25 g 13/3

Packages included

2:4:7-Trinitro-fluorenone



2:4:7-Trinitro-fluorenone, supplied as a pale yellow crystalline powder, melting point 175-6° C, forms stable complexes with a wide variety of aromatic hydrocarbons and derivatives. The complexes are readily prepared and generally melt sharply without decomposition. Apart from their use for identification, they can be employed in purifying certain aromatic hydrocarbons, since the hydrocarbon portion of the complex can be recovered by passing a solution of the complex over activated alumina. Alternatively, the complex may be reduced, giving an acid-soluble product from the trinitro-fluorenone moiety.

There are references in the literature to over a hundred substances known to form complexes with 2:4:7-trinitro-fluorenone. A bibliography will be supplied on application.

1 g 4/9 5 g 17/3 10 g 33/-

Packages included

THE BRITISH DRUG HOUSES LTD.
B.D.H. LABORATORY CHEMICALS GROUP
POOLE DORSET

MHT/LC/561g

Printed in Great Britain by Richard Clay and Company, Ltd., Bungay, Suffolk.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING MARCH, 1956

LONDON.

Thursday, March **15th, 1956,** *at* 6.30 *p.m.*

Reception and Conversazione. To be held in the Science Museum, South Kensington, S.W.7. (Further details will be circulated.)

ABERDEEN.

Friday, March **16th, 1956,** *at* 7.30 *p.m.*

Lecture, **Distinguished Men of Science living in Britain in 1807—1808,** by Dr. A. Clow, F.R.S.E. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at Marischal College.

BIRMINGHAM.

Friday, March **9th, 1956,** *at* 4.30 *p.m.*

Lecture, **Some Recent Trends in the Synthesis of Coloured Substances,** by Dr. H. T. Howard. Joint meeting with the University Chemical Society to be held in the Chemistry Department, The University.

BRISTOL.

Thursday, March, **1st, 1956,** *at* 5.15 *p.m.*

Lecture, **Tropylium,** by Professor M. J. S. Dewar, M.A., D.Phil. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday, March **8th, 1956,** *at* 7.0 *p.m.*

Lecture, **Fuel Practice in Italy,** by Professor C. Padovani. Joint Meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, and the Institute of Fuel, to be held in the Chemistry Department, The University.

Thursday, March **15th, 1956,** *at* 5.15 *p.m.*

Lecture, **Some Recent Developments in the Chemistry of the Vitamins D,** by Professor B. Lythgoe, M.A., Ph.D. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday March **22nd, 1956,** *at* 7.0 *p.m.*

Lecture, **Fluorescence Analysis in Ultraviolet Light,** by Mr. J. A. Radley, M.Sc., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

CAMBRIDGE.

Friday, March 2nd, 1956, at 8.30 p.m.

Lecture, **Some Recent Studies in the Fatty Acid Field,** by Dr. B. C. L. Weedon, B.Sc., A.R.I.C. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Pembroke Street.

EDINBURGH.

Thursday, March 15th, 1956, at 7.30 p.m.

Meeting for the Reading of Papers on **The Application of New Techniques to Some Problems in Brewing,** with contributions from Professor I. A. Preece, Mr. L. Fletcher, and Dr. J. O. Harris. To be held at the North British Station Hotel.

GLASGOW.

Friday, March 16th, 1956, at 7.15 p.m.

Meeting for the Reading of Original Papers. To be held in the Chemistry Department, The University.

HULL.

Thursday, March 1st, 1956, at 6 p.m.

Lecture, **Compounds of Lithium and their Use in Synthesis,** by Professor E. A. Braude, D.Sc., F.R.I.C., to be given in the Chemistry Department, The University.

IRISH REPUBLIC.

Friday, March 9th, 1956, at 7.45 p.m.

Lecture, **The Spontaneous Formation of Structure in Solutions of High Polymers,** by Dr. C. Robinson, B.Sc., F.R.I.C. Joint Meeting with the Werner Society to be held in the University Chemical Laboratory, Trinity College, Dublin.

LEEDS.

Monday, March 5th, 1956, at 6.30 p.m.

Royal Institute of Chemistry Lecture, **New Developments in Inorganic Chemistry,** by Professor R. S. Nyholm, D.Sc., A.R.I.C., to be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

Tuesday, March 13th, 1956, at 6.30 p.m.

Lecture, **Tropylium,** by Professor M. J. S. Dewar, M.A., D.Phil. Joint Meeting with Leeds University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

LIVERPOOL.

Thursday, March 22nd, 1956, at 5.0 p.m.

Lecture, **The Fructose Group of Polysaccharides,** by Professor E. L. Hirst, F.R.S. Joint Meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, the British Association of Chemists, and the University Chemical Society, to be held in the Chemistry Lecture Theatre, The University.

NEWCASTLE AND DURHAM.

Friday, March 2nd, 1956, at 4.0 p.m.

Meeting for the Reading of Original Papers. To be held in the Chemistry Building, King's College, Newcastle upon Tyne, 1.

NORTHERN IRELAND.

Tuesday, March 13th, 1956, at 7.45 p.m.

Meeting for the Reading of Original Papers. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at Queen's University, Belfast.

Thursday, March 22nd, 1956, at 7.15 p.m.

Lecture, **Some Themes in Chemotherapy,** by Dr. L. P. Walls, M.A. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemistry, to be held at The Queen's University, Belfast.

NOTTINGHAM.

Monday, March 5th, 1956, at 4.30 p.m.

Lecture, **Liquid Crystals,** by Professor Brynmor Jones, Ph.D., Sc.D., F.R.I.C. Joint Meeting with University College of Leicester Chemical Society to be held at University College, Leicester.

Monday, March 26th–Wednesday, March 28th, 1956.

Anniversary Meetings—a full programme will be circulated.

OXFORD.

Monday, March 5th, 1956, at 8.15 p.m.

Lecture, **Solid Imperfections and Chemical Reactivity,** by Dr. F. C. Tompkins, F.R.S. Joint Meeting with the Oxford University Alembic Club to be held in the Physical Chemistry Laboratory, South Parks Road, Oxford.

ST. ANDREWS AND DUNDEE.

Thursday, March 8th, 1956, at 5.0 p.m.

Lecture, **Chemical Engineering and its Place in the University,** by Professor K. G. Denbigh, Ph.D., F.R.I.C., to be given in the Chemistry Department, Queen's College, Dundee.

SHEFFIELD.

Thursday, March 8th, 1956, at 7.30 p.m.

Lecture, **Transitions in Ammonium Salts,** by Mr. L. A. K. Staveley, M.A. Joint Meeting with the University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

SOUTHAMPTON.

Friday, March 2nd, 1956, at 5.0 p.m.

Lecture, **Cationic Polymerisation,** by Professor A. G. Evans, M.Sc., Ph.D. Joint Meeting with Southampton University Chemical Society to be held in the Chemistry Department, The University.

Friday, March 16th, 1956, at 5.0 p.m.

Lecture, **Gas-phase Chromatography,** by Dr. A. T. James. Joint Meeting with Southampton University Chemical Society to be held in the Chemistry Department, The University.

Wednesday, March 21st, 1956, at 7.0 p.m.

Lecture, **Some Recent Developments in the Chemistry of Free Radicals,** by Professor D. H. Hey, D.Sc., F.R.I.C., F.R.S. Joint Meeting with Portsmouth and District Chemical Society and the Royal Institute of Chemistry, to be held at the College of Technology, Anglesea Road, Portsmouth.

SOUTH WALES.

Monday, March 5th, 1956, 5.30 p.m.

Lecture, **Melting and Crystal Structure,** by Professor A. R. Ubbelohde, M.A., D.Sc., F.R.S. To be given in the Department of Chemistry, University College, Cardiff.

Friday, March 9th, 1956, at 5.30 p.m.

Lecture, **Some Recent Developments in the Chemistry of Free Radicals,** by Professor D. H. Hey, D.Sc., F.R.I.C., F.R.S. To be given in the Chemistry Department, University College, Swansea.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Jack Eldred Brimley (East Didsbury)	May 6th, 1948.	July 7th, 1954.
Francis Hereward Burstall (Teddington)	Dec. 3rd, 1925.	Dec. 2nd, 1955.
Sir Wilfred Russell Grimwade (Melbourne)	Dec. 4th, 1902.	Nov. 2nd, 1955.
William Jay Hale (Michigan)	May 2nd, 1918.	1955.
Charles King (Glasgow)	Dec. 2nd, 1925.	Sept. 16th, 1955.
Ralph William Ewart Stickings (Brentwood) ...	Mar 1st, 1919.	Dec. 3rd, 1955.
Herbert Ernest Williams (Hyde)	Dec. 2nd, 1909.	Nov. 15th, 1955.
Robert Harding Williams (Hull)	Dec. 3rd, 1925.	Oct. 8th, 1955.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to Sir Cyril Hinshelwood on his election as President of the Royal Society.

Congratulations have also been conveyed to the following Fellows who completed 60 years of Fellowship on December 5th, 1955:

James Henderson (Dundee).
Clarence Arthur Seyler (Leatherhead).

and to the following who completed 50 years of Fellowship on December 7th, 1955:

Joseph Edward Coates (Swansea).
Arthur Augustine Dallman (Doncaster).
Herbert Drake Law (London, E.15).

ELECTION OF NEW FELLOWS.

The following 65 candidates were elected to the Fellowship on December 15th, 1955:

John Napier Andrews.
Mehkeri K. Anwer.
Edward McCollin Arnett.
Bryan Webb Ashton.
Andrew Balsillie.
Derek Victor Banthorpe.
Jeffrey John Batten.
Peter Desmond Blundy.
Sidney John Branch.
Leonard George Bray.
Herbert Buchwald.
James Robertson Burt.
Henry Stowar Burton.
David Trevor Bushman.
Hugh Bernard Charman.
Peter Edward Curry.
Michael Charles Dart.
John Graham Dawber.
Gabriel Paschal Fazi.
Ramsis Gobran.
Drago Grdenic.
Francis Robert Frederick Hardy.
Derek Harrison.
Ian Thomas Harrison.
Jeremy Robin Harrold.
John Evan Hazell.
Robert Enys Hichens.
Hiroo Inokuchi.
Herbert David Kaesz.
Michael Kennedy.
Gordon William Kirby.
Robert Letters.
John Stanley Little.
John J. Lucier.
Kenneth James Macleod.
Hyman Dave Massin.
John Newbould.
Primula Anne Newton-Hearn.
David Nicholls.
Peter Norton.
Sidney Bertram Phillips.
Geoffrey Pilcher.
Norman Edward Ransome.
Edward Arthur Robinson.
Andrzej Rozanski.
Gopal Rao Savur.
John Antony Schofield.
Promode Prakash Shrivastav.
Osamu Simamura.
Frank Skuse.
Brian Robson Smith.
Peter Trafford Speakman.
Sanae Tanaka.
Brian Leslie Taylor.
Malcolm James Thompson.
John Graham Tillett.
John Francis James Todd.
Peter Douglas Trethewey.
Kenneth Holmes Turner.
Douglas Hugh Watson.
Peter Jaffrey Wheatley.
Grosvenor Searles Wich.
John Colin Williams.
David Jankiel Wluka.
Keith Henry Wood.

RESEARCH FUND.

The Council has approved the following grants from the Research Fund:

	£	s.	d.
Baker, W. (Bristol)	21	8	0
Blair, J. A. (Achimota, Gold Coast)	50	0	0
Eaborn, C. (Leicester)	40	0	0
Evans, A. G. (Cardiff)	30	0	0
Fowles, G. W. A. (Southampton)	25	8	4
Greenwood, N. N. (Nottingham)	25	0	0
Hough, L. (Bristol)	40	0	0
Jones, G. (Keele)	9	0	0
Khundkar, M. H. (Pakistan)	25	0	0
Kurzer, F. (London)	15	0	0
Landor, S. R. (London)	20	0	0
Millar, I. T. (Keele)	8	6	8
Overend, W. G. (London)	22	10	0
Paul, R. C. (India)	51	0	0
Powell, D. B. (London)	27	0	0
Raphael, R. A. (Belfast)	30	0	0
Rottenberg, M. (Switzerland)	15	0	0
Salmon, J. E. (London)	25	0	0
Stock, D. I. (London)	20	0	0
Stranks, D. R. (Leeds)	42	0	0
Taylor, H. (Portsmouth)	20	0	0
Thomson, S. J. (Durham)	23	0	0
Trotman-Dickenson, A. F. (Edinburgh)	40	0	0
Voaden, D. J. (Oxford)	10	0	0
Walsh, A. D. (Dundee)	33	10	6

CHANGES IN LIBRARY REGULATIONS.

Changes in the regulations of the Chemical Society Library have been approved. The principal changes are as follows:

1. The closing time for the period October to July will be 7.30 p.m. instead of 9 p.m. (Saturdays 5 p.m.)
2. The period of loan is reduced from one month to fourteen days, but can be extended upon request.
3. All periodical material is now available for loan whether held in duplicate or not, subject to the discretion of the Librarian.

A copy of the revised regulations may be obtained from the Librarian.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at the Royal Institution, Albemarle Street, London, W.1, on Thursday, December 1st, 1955, at 7.30 p.m.

Professor C. K. Ingold, D.Sc., F.R.S., Vice-President, was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at the Imperial College of Science and Technology on November 17th, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: E. W. R. Steacie, M. G. Ford, J. M. Batstone, E. A. Simpson, E. W. Hammond, R. C. B. Tomlinson, J. R. Young, M. A. Whitehead, S. W. Gilks, P. A. Bosanquet.

LIVERSIDGE LECTURE.

The Chairman called upon Dr. E. W. R. Steacie, O.B.E., M.Sc., F.R.S., to deliver the Liversidge Lecture entitled "Reactions of Radicals in Gaseous Systems." At the conclusion of the Lecture a vote of thanks to Dr. Steacie, proposed by Professor D. H. Hey, D.Sc., F.R.S, was carried with acclamation.

Minutes of a

SCIENTIFIC MEETING

held at Burlington House, on Thursday, December 15th, 1955, at 7.30 p.m.

The President, Professor W. Wardlaw, C.B.E., D.Sc., F.R.I.C., was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at the Royal Institution on Thursday, December 1st, 1955, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: E. McLaughlin, L. E. Addy, A. A. Williams, G. A. Gamlen, P. F. Todd, J. M. C. Thompson.

SCIENTIFIC COMMUNICATIONS.

The following papers were read and discussed:

"Delocalised Metal–Carbon Bonds." By L. E. Orgel.

"Complexes of Uncharged Aromatic Systems with Transition Metals and the Bonding Problem of Ferrocene and Similar Compounds." By E. O. Fischer. (Techn. Hochschule, München.)

"Ferrocene Derivatives. Part III. Ferrocene Dicarbonyl and Related Compounds." By B. F. Hallam and P. L. Pauson.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretary within ten days of the date of publication of the Journal *for January. 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Adcock, Brian. British. 137, Pear Tree Crescent, Derby. Student at Queen's College, Oxford. *Signed by:* L. A. K. Staveley, J. W. Linnett.

Andrews, Anthony Leonard. British. 31, High Street, Brighouse, Yorks. Undergraduate. *Signed by:* L. A. K. Staveley, R. J. P. Williams.

Arnold, Richard Bentham, B.Sc. (Nott.). British. Department of Chemistry, The University, Nottingham. Research Student. *Signed by:* C. C. Addison, T. J. King.

Barnden, Roy Leonard. British. 25, The Poynings, Richings Park, Iver, Bucks. Research and Development Chemist. *Signed by:* A. J. Krajkeman, A. Coenders.

Barnes, Terence John. British. 57, Silver Lane, West Wickham, Kent. Student at Queen Mary College, London. *Signed by:* M. J. S. Dewar, R. F. Garwood.

Chapman, Derek David, B.Sc. (Nott.). British. Chemistry Department, The University, Nottingham. Research Student. *Signed by:* C. C. Addison, M. W. Partridge.

Clayton, Jeffrey Colin, B.Sc. (Nott.). British. **48,** Wymington Road, Rushden, Northants. Instructor Lieutenant, Royal Navy. *Signed by:* C. C. Addison, J. E. Davies.

Cleaver, Brian. British. **138,** Middlemore Road, Northfield, Birmingham, **31.** Student at Magdalen College, Oxford. *Signed by:* L. A. K. Staveley, L. E. Sutton.

Davies, Hugh Edryd Joshua. British. **9,** Aldenham Road, Newton, Porthcawl, Glam. Undergraduate at Brasenose College, Oxford. *Signed by:* J. A. Barltrop, L. A. K. Staveley.

Durham, Lois Jean, B.S. (Calif.). American. Department of Chemistry, Stanford University, Stanford, California, U.S.A. Graduate Student, Teaching Assistant. *Signed by:* M. Look, H. Rapoport.

Easton, Brian Colin, B.Sc. (Lond.). British. **171,** Wickham Street, Welling, Kent. Research Student. *Signed by:* H. Burton, M. K. Hargreaves.

Gimblett, Frederick Gareth Robert, M.Sc. (Wales). British. Chemistry Department, Royal Aircraft Establishment, Farnborough, Hants. Research Chemist at the Ministry of Supply. *Signed by:* G. M. Bristow, E. J. P. Fear.

Godwin, Michael Francis Harold. British. The Rectory, Heyshott, Midhurst, Sussex. Student at Nottingham University. *Signed by:* C. C. Addison, F. C. Laxton.

Hall, Gordon Edwin, B.A. (Cantab.). British. **4,** Cundalls Road, Ware, Herts. Research Student at Cambridge University. *Signed by:* D. M. Brown, J. J. Wren.

Handisyde, Jill. British. St. Wilfreds, Shootersway Lane, Berkhamsted, Herts. Undergraduate at Oxford University. *Signed by:* L. A. K. Staveley, M. L. Tomlinson.

Hanson, James Ralph. British. **31,** Station Road, New Barnet, Herts. Student. *Signed by:* L. A. K. Staveley, J. A. Barltrop.

Harwood, Geoffrey Ellis. British. **24,** Winchester Drive, Pinner, Middlesex. Student at Southampton University. *Signed by:* N. B. Chapman, E. A. S. Cavell.

Hell, Anna Elisabeth. British. **3,** Eldon Grove, London, N.W.3. Student at Somerville College, Oxford. *Signed by:* L. A. K. Staveley, R. E. Richards.

Higson, Helen Margaret, B.A. (Cantab.). British. **13,** Ragworth Place, Norton, Stockton-on-Tees. Research Chemist with Shell Research, Ltd. *Signed by:* J. Yates, F. H. Newth.

Hollander, Jerome, B.A. (New York). American. Chemistry Department, University of North Carolina, Chapel Hill, North Carolina, U.S.A. Graduate Student. *Signed by:* J. F. Bunnett, D. B. Bright.

Hollinghurst, Ralph. British. Keble College, Oxford. Student. *Signed by:* L. A. K. Staveley, G. D. Parkes.

Hurdman, Gillian Iris Mary. British. **37,** Vicarage Road, Yardley, Birmingham, **33.** Undergraduate at St. Hilda's College, Oxford. *Signed by:* L. A. K. Staveley, M. L. Tomlinson.

Jackson, Colin, B.Sc. (Dunelm). British. **17,** Bideford Gardens, Low Fell, Gateshead, **9,** Co. Durham. Research Student. *Signed by:* G. A. Swan, H. Marsh.

Jones, John Royston, B.Sc. (Wales), A.R.I.C. British. Bristol House, Cefn Road, Blackwood, Monmouthshire. Research Student at Cardiff University. *Signed by:* J. W. Bayles, N. Thorne.

Jones, Raymond Arthur. British. **21,** Haddon Grove, Sidcup, Kent. Analytical Chemisty. *Signed by:* J. R. Barr, H. Green.

Khin, Aung, B.Sc. (Lond.), B.Sc. (Rangoon). Burmese. **14,** Aungthabye Street, Sangyaung, Rangoon, Burma. Student. *Signed by:* A. I. Vogel, G. H. Jeffery.

Kubota, Takashi, Dr.Sc. (Osaka). Japanese. c/o The Institute of Polytechnics, Osaka City University, 12 Minami-Ogimachi, Kitaku, Osaka, Japan. Professor of Organic Chemistry. *Signed by:* S. Murahashi, T. Sakan.

Mallett, Kenneth George. British. **35,** Hunter's Lane, Richmond, Sheffield, **13.** Undergraduate at Queen's College, Oxford. *Signed by:* L. A. K. Staveley, J. W. Linnett.

Mayuranathan, Puthamkurichi Subramanyaiyer, B.A. and M.Sc. (Madras). Indian. Maharaja's College, Ernakulam, S. India. Professor of Chemistry. *Signed by:* K. Venkataraman, C. K. Ingold.

Mee, Alec, B.Sc. (Liv.). British. Tweenways, Beckintch Lane, Belper, Derbyshire. Demonstrator at Liverpool University. *Signed by:* W. B. Whalley, A. McGookin.

Mester, Laszlo, D.Chem.Eng. (Budapest Tech. Univ.). Hungarian. Krisztina krt. 45, Budapest I., Hungary. Lecturer and Assistant Professor at the Techn. Univ. Budapest. *Signed by:* J. Kovacs, Z. Foldi.

Miller, John Alfred. British. **468,** London Road, Davenham, Nr. Northwich, Cheshire. Student at Hull University. *Signed by:* G. W. Gray, K. Clarke.

Mulay, Laxman N., M.Sc. and Ph.D. (Bombay), A.R.I.C. Indian. Department of Chemistry, Harvard University, 12, Oxford Street, Cambridge **38,** Massachusetts, U.S.A. Research Fellow. *Signed by:* R. E. Glick, F. G. A. Stone.

Nakamichi, Masumi, B.S. (Illinois). American. **428,** North Noble Street, Chicago 22, Illinois, U.S.A. Graduate Student at the University of Illinois. *Signed by:* R. Daniels, L. Bauer.

Norton, Albert, M.A. and B.Sc. (Oxon.), F.R.I.C. British. Rowntree and Co. Ltd., The Cocoa Works, York. Manager, Products Research and Development Department. *Signed by:* E. E. Wells, F. S. Dainton.

Otter, Raymond James, B.Sc. (Reading). British. **22,** Warwick Road, Reading, Berks. Research Student at Reading University. *Signed by:* C. L. Leese, J. E. Prue.

Peel, Mervyn Evan, M.Sc. (Lond.). British. **45,** St. Margarets, Stanstead Abbotts, Nr. Ware, Herts. Research Chemist with Allen and Hanbury's Ltd., Ware. *Signed by:* E. P. Taylor, J. H. Hunt.

Perriman, Rodney John. British. 38, Featherby Road, Gillingham, Kent. Student at Southampton University. *Signed by:* N. B. Chapman, E. A. S. Cavell.

Pitches, Marion Doreen. British. 17, Northcote Avenue, Ealing, London, W.5. Student. *Signed by:* W. J. Hickinbottom, D. M. Grove.

Potter, David John Bretton, B.Sc. (Reading). British. 28, Balmore Drive, Caversham, Reading, Berks. Postgraduate Research Student at Reading University. *Signed by:* C. L. Leese, J. E. Prue.

Rogers, Terence Edward. British. 15, Shaftesbury Road, Southsea, Hants. Student at Queen Mary College, London, *Signed by:* R. F. Garwood, D. M. Grove.

Roth, Barbara, M.S. and Ph.D. (Northwestern). American. The Wellcome Research Laboratories, Tuckahoe 7, New York, U.S.A. Senior Research Chemist. *Signed by:* P. B. Russell, G. B. Elion, G. H. Hitchings.

Rothery, Edward Joseph, B.Sc. (U.C.D.). Irish. 109, Thomas Street, Dublin. Assistant Distiller, John Power and Son, Ltd. *Signed by:* P. F. Devitt, J. E. Gowan.

Ryan, Adrian John, B.Sc. (Sydney). British. Flat 1, 65, Fletcher Street, Bondi, N.S.W., Australia. Teaching Fellow. *Signed by:* A. J. Birch, R. J. W. Le Fèvre, A. V. Robertson.

Scott, John James, M.A. (Cantab.). Ph.D. (Lond.). British. Department of Chemical Pathology, St. Mary's Hospital Medical School, Paddington, London, W.2. Research Worker and Lecturer. *Signed by:* A. Neuberger, C. E. Dalgliesh.

Skinner, Leonard Harold. British. 15, Canonbury Lane, Islington, London, N.1. Student at Queen Mary College, London. *Signed by:* M. J. S. Dewar, R. F. Garwood.

Sklarz, Benjamin. British. 36, Amhurst Park, London, N.16. Student. *Signed by:* F. G. Mann, A. G. Sharpe.

Spainhour, James Dudley, B.S. (N. Carolina). American. 3206, Crestwood Lane, Glenview, Illinois, U.S.A. Graduate Student at Northwestern University. *Signed by:* F. G. Bordwell, F. Basolo.

Stone, James Bryan, B.Sc. (Lond.). British. 30, Wilson Avenue, Summit, Heywood, Lancs. Research Student at Queen Mary College, London. *Signed by:* M. F. Ansell, R. F. Garwood.

Tapping, Kenneth George. British. 39, Maidcroft Road, Cowley, Oxford. Student at Oxford University. *Signed by:* L. A. K. Staveley, A. S. Bailey.

Trotter, James, B.Sc. (Glas.). British. 32, Banavie Road, Glasgow, W.1. Assistant Lecturer. *Signed by:* D. S. Payne, J. C. Speakman.

Varma, Jyoti Prasad, M.Sc. (Luck.), A.R.I.C. Indian. National Chemical Laboratory, Poona-8, India. Research Chemist. *Signed by:* G. I. Finch, R. C. Shah.

Vredenburgh, Walter Anthony, M.A. (Wisconsin). American. 854, Terry Place, Madison 5, Wisconsin, U.S.A. Research Assistant at the University of Wisconsin. *Signed by:* W. S. Johnson, S. M. McElvain.

Waghorn, Michael John, A.R.I.C. British. 14, Wexham Road, Slough, Bucks. Research Chemist with I.C.I. Paints Division, Slough. *Signed by:* H. Brunner, D. J. Walbridge.

Walker, Derek, B.Sc. (Lond.), Ph.D. (Leeds), A.R.I.C. British. 55, County Road South, Willerby Road, Hull, Yorks. Research Chemist at the United Kingdom Atomic Energy Authority. *Signed by:* G. I. Gregory, A. J. S. Sorrie.

Wijesekera, Rahula Oliver Barnes, B.Sc. (Ceylon), A.R.I.C. Ceylonese. Department of Chemistry, The University, Sheffield, 10. Research Student. *Signed by:* J. Grimshaw, P. L. Pauson.

Wise, David Victor, B.Sc. (Lond.). British. 180, Skipton Road, Keighley, Yorks. Research Student at Queen Mary College, London. *Signed by:* M. F. Ansell, R. F. Garwood.

Wooldridge, John Raymond, B.A. (Cantab.). British. Bentley Hyde, Priory Drive, Stanmore, Middlesex. Research Student at Birkbeck College, London. *Signed by:* W. G. Overend, C. W. Rees.

Zayed, Salah Mohamed Abdel Dayem, M.Sc. (Cairo). Egyptian. Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt. Demonstrator. *Signed by:* M. I. Ali, M. Kamel.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Agarwal, Om Prakash, M.Sc. (Allahabad), B.T. (Bombay). Indian. Mahmud School, Raub, Pahang, Malaya. Senior Science Master. *Signed by:* R. A. Robinson.

Blum, Dieter Wolfgang, Dipl. Chem. (Heidelberg). German. Mundenheimerstr. 168, (22b) Ludwigshafen a.Rh., Germany. Chemist. *Signed by:* R. Kuhn.

Nery, Raghoonandan, B.Sc. (Muhlenberg), Ph.D. (Lond.), A.R.I.C. British. George Herbert Jones Laboratory, Rm. 322, University of Chicago, Chicago 37, Illinois, U.S.A. Post-doctoral Research. *Signed by:* V. A. Williams.

Seymour, Keith Morton, M.S. and Ph.D. (Washington). American. Butler University, Indianapolis 7, Indiana, U.S.A. Professor and Head of Department of Chemistry. *Signed by:* A. H. Fiske.

Venkaji, Krishnaswamy, M.A. and M.Sc. (Annamalai). Indian. Salt Test Laboratory, Tondiarpet, Madras 21, India. Chemical Assistant. *Signed by:* V. Baliah.

Zifferero, Maurizio, Dr. Chem. (Rome). Italian. Istituto di Chimica Farmaceutica dell'Universita, Rome, Italy. Assistant in pharmaceutical chemistry. *Signed by:* G. Giacomello.

PAPERS ACCEPTED

(List of Papers accepted between November 28th, 1955, and December 5th, 1955, for publication in the *Journal*.)

"Aliphatic hydroxylamines. Part II. Autoxidation." By DAVID H. JOHNSON, M. A. THOROLD ROGERS, and G. TRAPPE.

"The synthesis of 5-pyrimidinyl sulphides and disulphides. Part II." By G. R. BARKER and NYDIA G. LUTHY.

"Mechanism of substitution at a saturated carbon atom. Part L. Kinetic effects of phenyl and halogen substituents in alkyl halides on their reactions with halide ions in acetone." By P. B. D. DE LA MARE and E. D. HUGHES.

"Mechanism of substitution at a saturated carbon atom. Part LI. *ortho*-Effects in solvolysis of arylalkyl halides, illustrating steric retardation in a unimolecular substitution." By J. C. CHARLTON and E. D. HUGHES.

"Mechanism of substitution at a saturated carbon atom. Part LII. Polar and steric *ortho*-effects in bimolecular Finkelstein substitutions of arylalkyl halides." By J. C. CHARLTON and E. D. HUGHES.

"Conductometric studies in ketonic solvents. Part II. Water in ketones." By S. R. C. HUGHES.

"Organic fluorine compounds. Part VI. The enolates of alkyl fluoroacetates." By ERNST D. BERGMANN and S. SZINAI.

"Organic fluorine compounds. Part VII. The Perkin and similar reactions with fluoroacetic acid." By ERNST D. BERGMANN and JOSE SCHWARCZ.

"The oxidation of hydrocarbons and their derivatives. Part I. The observation of the progress of the reaction by pressure change and by analysis." By B. I. PARSONS and C. J. DANBY.

"The oxidation of hydrocarbons and their derivatives. Part II. Structural effects in the ester series." By B. I. PARSONS and SIR CYRIL HINSHELWOOD.

"The oxidation of hydrocarbons and their derivatives. Part III. The rôle of intermediates." By B. I. PARSONS.

"Tracer studies on ester hydrolysis. Part III. The alkaline hydrolysis of phenyl benzoate." By C. A. BUNTON and D. N. SPATCHER.

"The ammonolysis of methyl 2 : 3-anhydro-D-furanosides. Part II. Methyl 2 : 3-anhydro-5-*O*-methyl-α- and -β-D-lyxofuranosides." By J. M. ANDERSON and ELIZABETH PERCIVAL.

"The allomerization of chlorophyll." By L. G. JOHNSTON and W. F. WATSON.

"The thermal decomposition of octadeutero*cyclo*butane and octafluoro*cyclo*butane." By B. F. GRAY and H. O. PRITCHARD.

"Long-range effects in alicyclic systems. Part I. The rates of rearrangement of some steroidal dibromides." By D. H. R. BARTON and A. J. HEAD.

"Kinetic studies in the phosphinyl chloride and phosphorochloridate series. Part V. Evidence for a one-stage mechanism in the hydrolysis of diethyl phosphorochloridate." By I. DOSTROVSKY and M. HALMANN.

"Some new tropine derivatives." By R. FOSTER and H. R. ING.

ADDITIONS TO THE LIBRARY

The item marked with an asterisk (*) is for reference only.

BRAME, J. S. S., and KING, J. G. **Fuel: solid, liquid, and gaseous. 5th edn. 1955. Edward Arnold. 50*s*.**

BRITTON, H. T. S. **Hydrogen ions: their determination and importance in pure and industrial chemistry. 4th edn. Vol. 1. 1955. Chapman and Hall. 70*s*.**

BURNS, R. M., and BRADLEY, W. W. **Protective coatings for metals. 2nd edn. 1955. (American Chemical Society Monograph Series, No. 129.) Reinhold. 96*s*.**

DANIELS, F., and ALBERTY, R. A. **Physical chemistry. 1955. Wiley. 52*s*.**

*FERRIS, S. W. **Handbook of hydrocarbons. 1955. Academic Press. 68*s*.**

FLECK, H. R. **Synthetic drugs: a handbook for chemists, physicians, and pharmacists. 1955. Cleaver-Hume. 70*s*.**

FRANCIS, W. **Boiler house and power station chemistry. 3rd edn. 1955. Edward Arnold. 50*s*.**

13TH INTERNATIONAL CONGRESS OF PURE AND APPLIED CHEMISTRY. **Stockholm, 1953. Abstracts of papers. 1953. Almquist & Wiksell. 45*s*.**

LEES, H. **Biochemistry of autotrophic bacteria. 1955. Butterworths. 21*s*.**

LI, K. C., and CHUNG YU WANG. **(Eds.) Tungsten. 3rd edn. (American Chemical Society Monograph Series, No. 94.) 1955. Reinhold. 112*s*.**

LINSTEAD, R. P., ELVIDGE, J. A., and WHALLEY, M. **A course in modern techniques of organic chemistry. 1955. Butterworths. 25*s*.**

LOWE, B. **Experimental cookery from the chemical and physical standpoint. 4th edn. 1955. Wiley. 60*s*.**

Proceedings of the 6th meeting of the International Committee of Electrochemical Thermodynamics and Kinetics, Poitiers, 1954. 1955. Butterworths. 84*s*.

The Roger Adams symposium. 1955. Wiley. 30*s*.

SCHMIDT, J. **A text-book of organic chemistry. 7th edn. (Revised and edited by N. Campbell.) 1955. Oliver and Boyd. 35*s*.**

SOCIETY FOR EXPERIMENTAL BIOLOGY. **Fibrous proteins and their biological significance. (Symposia of the Society for Experimental Biology, No. 9.) 1955. Cambridge Univ. Pr.**

(Presented by A. L. Bacharach.)

STANDING COMMITTEE ON COMBUSTION SYMPOSIA. **Fifth symposium (international) on combustion; combustion in engines and combustion kinetics. 1955. Reinhold. 108*s*.**

TOWNES, C. H., and SCHAWLOW, A. L. **Microwave spectroscopy. 1955. McGraw-Hill. 84*s*.**

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	Dr. K. H. Pausacker, Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc, Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, Research Department, Widnes Laboratory, Widnes.
Manchester.	G. R. Barker, B.Sc., Ph.D., Chemistry Department, The University, Manchester, 13.
,,	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
Newcastle and Durham.	G. A. Swan, D.Sc., Ph.D., F.R.I.C., Department of Chemistry, King's College, Newcastle-on-Tyne, 1.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, PhD., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham.	C. C. Addison, D.Sc., Ph.D., F.R.I.C., Chemistry Department, The University, University Park, Nottingham.
Oxford.	L. A. K. Staveley, M.A., Inorganic Chemistry Laboratory, South Parks Road, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A.R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	K. W. Sykes, M.A., B.Sc., D.Phil., Department of Chemistry, University College, Singleton Park, Swansea.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

ANNIVERSARY MEETINGS

Monday, March 26th—Wednesday, March 28th, 1956.

Full details of the Anniversary Meetings to be held in Nottingham have been issued as a separate notice.

SCIENTIFIC MEETINGS DURING APRIL, 1956

BRISTOL.

Thursday, April 26th, 1956, at 5.15 p.m.

Lecture, **Magnetism and the Shape of Inorganic Molecules,** by Professor R. S. Nyholm, D.Sc., A.R.I.C. Joint Meeting with the Student Chemical Society, to be held in the Chemistry Department, The University.

IRISH REPUBLIC.

Wednesday, April 18th, 1956, at 7.45 p.m.

Lecture, **The Organisation of Intracellular Reactions,** by Mr. F. Winder, M.Sc. To be given in the Chemistry Department, University College, Dublin.

MANCHESTER.

Thursday, April 19th, 1956, at 10.30 a.m. to 6.30 p.m.

Symposium, **Lubrication.** Joint Meeting with the Institute of Petroleum, the Royal Institute of Chemistry, and the Society of Chemical Industry, to be held in the Large Chemistry Theatre, The University.

NORTHERN IRELAND.

Thursday, April 19th, 1956, at 7.45 p.m.

Lecture, **Adsorption by Porous Solids,** by Professor D. H. Everett, M.B.E., M.A., D.Phil. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at The Queen's University, Belfast.

ST. ANDREWS AND DUNDEE.

Friday, April 13th, 1956, at 5.15 p.m.

Lecture, **A New Chemistry,** by Dr. R. N. Haszeldine, B.Sc. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, St. Salvators College, St. Andrews.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows :

	Elected.	Died.
David Runciman Boyd (Fordingbridge) (C. 1924—27)	Dec. 6th, 1894.	Dec. 28th, 1955.
James Lewis Howe (Lexington, Va.)	Dec. 7th, 1882.	Dec. 20th, 1955.
James Howard Linday (Beeston)	June 17th, 1903.	Dec. 12th, 1955.
Michael Selleck (Egham)	July 15th, 1954.	Dec. 15th, 1955.
Frank Sherwood Taylor (Crowthorne)	Feb. 18th, 1926.	Jan. 1st, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows whose names appeared in the New Year Honours List :

D.B.E.

Kathleen Lonsdale (London, W.C.1).

C.B.E.

Cecil Edwin Henry Bawn (Liverpool).

ELECTION OF NEW FELLOWS.

The following 81 candidates were elected Fellows of the Society on January 19th, 1956 :

Douglas Einar Applequist.
Burton Lawrence Appleton.
John Arthur Baldrey.
Ian Knowles Barben.
John Bolton Bird.
Sydney Kenneth Brownstein.
Ernest E. Campaigne.
Gino Carrara.
Eugene Anthony Cherniak.
Arthur Kenji Cho.
Basil James Frederick Christie.
David Cohen.
Graham Frederick Cox.
Harry Roscoe Cross.
John Edward Downes.
John William Ducker.
Stanley Frederick Dyke.
Ronald Sydney Fielder.
John Michael Foster.
Andre Goosen.
Hylton Judith Grenville-Wells.
Claibourne Eugene Griffin.
Ronald James Gutteridge.
Anthony Richard Hands.
Albert Montagu Harper.
Frances Rose Harper.
Robert John High.
George Holzman.
Ray Clyde Houtz.
Minoru Imoto.
William James Jackson.
Frank Llewellyn Jenkins.
Peter Kennedy.
Herbert Harold Keppler.
Alan Hodgson Laird.
Sandra Ina Lamb.
Joseph Lionel Latham.
David Lavie.
Joseph M. F. Leaper.
Derek Leaver.
John William Lee.
Richard James Mardell.
James Frederick Marten.
Takeshi Matsumoto.
Walter Maya.
Sydney Middleton.
Michael Charles Miller.
Philip Molyneux.
Ronald Haywood Moore.
Terence Michael Moynehan.
Masazimu Nakagawa.
S. Neelakantan.
Joan Dorothy Popkin.
Dennis Thornton Price.
Robert Puckowski.
Alan Trevor Radcliffe.
Svein Ramstad.
John Leslie Randall.
Gudipaty Sreenivas Rao.
Peter John Richardson.
Thomas Riley.
Michael John Temple Robinson.
Alan Rowland Rogers.
Louis Herman Rombach.
Carol Kilbourne Sauers.
Joseph Henry Scherrer.
Louis Herbert Schwartzman.
Mohammad Shafiq.
Dennis Sherman.
Edwin Julian Sparrow.
Roy Neville Speake.
John Alfred Stone.
Robert Louis Stutz.
Noboru Sugiyama.
George Sutherland Tait.
Alan John Vosper.
Helmut Weigel.
Leslie Edward West.
John Wilkinson.
Shou Yao Yeh.
Yasuhide Yukawa.

ACTA METALLURGICA.

Fellows are reminded that they may subscribe to *Acta Metallurgica* at the privileged rate of £3 6s. per annum. Renewal subscriptions by Fellows of The Chemical Society for 1956 may be sent direct to: The Secretary, The Institute of Metals, 4 Grosvenor Gardens, London, S.W.1.

Subscriptions from Fellows who have not previously received this journal should, in the first instance, be sent to: The General Secretary, The Chemical Society, Burlington House, London, W.1.

All orders, whether renewal or new subscriptions, should be accompanied by a remittance to cover the privileged subscription rate of £3 6s. per annum. Cheques should be made payable to "The Institute of Metals" in all cases.

PERKIN CENTENARY CELEBRATION.

The discovery of the first synthetic dyestuff by William Perkin is to be celebrated by a Conference and social functions from 7th to 10th May, 1956.

The Celebration is being sponsored by the Royal Society, the Chemical Society, the Society of Chemical Industry, the Society of Dyers and Colourists, the Royal Institute of Chemistry, and the Association of British Chemical Manufacturers.

The General Secretary of the Centenary Committee is Mr. J. W. Nicholls, c/o The Society of Dyers and Colourists, 19 Piccadilly, Bradford.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held in the Large Chemistry Lecture Theatre, Imperial College of Science and Technology, South Kensington, London, S.W.7, on Thursday, January 19th, 1956, at 7.30 p.m.

The President, PROFESSOR W. WARDLAW, C.B.E., D.Sc., F.R.I.C., was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at Burlington House on December 15th, 1955, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: Derek C. Burke, Gabriel P. Fazi, Neil R. Williams, Walter J. Le Quesne, John S. Nicholson, R. Ian T. Cromartie, Enid Gillian Holmes, John S. Little, R. C. Sheppard, R. H. McDowell, Nathan C. Hindley, and Barbara M. G. Pratt.

TILDEN LECTURE.

The President called upon Dr. G. W. Kenner, M.Sc., to deliver the Tilden Lecture entitled "Recent Progress in the Chemistry of Peptides." At the conclusion of the Lecture, a vote of thanks to Dr. Kenner, proposed by the President, was carried with acclamation.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretary within ten days of the date of publication of the Journal *for February, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Acton, Edward McIntosh, B.S. (Stanford). American. 382, Marlborough Street, Boston 15, Massachusetts, U.S.A. Student at Massachusetts Institute of Technology. *Signed by:* A. C. Cope, H. O. House.

Aghoramurthy, Krishna Sastri, B.Sc. (Madras), M.Sc. and Ph.D. (Delhi). Indian. Dyson Perrins Laboratory, South Parks Road, Oxford. 1851 Exhibition Scholar. *Signed by:* L. A. K. Staveley, H. Smith.

Augustine, Robert Leo, B.S. (Creighton), M.A. (Columbia). American. Department of Chemistry, Havemeyer Hall, Columbia University, New York, N.Y., U.S.A. Student. *Signed by:* G. Stork, R. A. L. Wilson.

Baldwin, Brian Charles. British. 70, Vanbrugh Park, Blackheath, S.E.3. Student. *Signed by:* M. J. S. Dewar, R. F. Garwood.

Banfield, James Edmund, M.Sc. and Ph.D. (Melbourne). British. 87, Rusden Street, Armidale, New South Wales, Australia. Lecturer. *Signed by:* N. V. Riggs, F. B. Dudley.

Barber, Michael. British. 166, Lodge Lane, Hyde, Cheshire. Undergraduate at Queen's College, Oxford. *Signed by:* L. A. K. Staveley, J. W. Linnett.

Birt, Lindsay Michael, B.Ag.Sc. and B.Sc. (Melbourne). Australian. Department of Biochemistry, University of Melbourne, Victoria, Australia. Student. *Signed by:* K. H. Pausacker, J. G. Scroggie.

Brain, Edward George, B.Sc. (Lond.). British. 4, Burton Road, London, S.W.9. Research Student. *Signed by:* A. B. Simmonds, I. L. Finar.

Braunholtz, John Theodore, M.A. and Ph.D. (Cantab.). British. 38, Trinity Street, Cambridge. Research Fellow at Trinity College. *Signed by:* F. G. Mann, R. N. Haszeldine.

Bullock, Eric, B.A. (Cantab.). British. 22, Woldcarr Road, Hull, Yorks. Research Student at Nottingham University. *Signed by:* A. W. Johnson, W. E. Addison.

Cade, Joseph Anthony, B.Sc. and Ph.D. (Lond.). British. 27, Dog Kennel Lane, Langley, Oldbury, Birmingham. Research Chemist. *Signed by:* H. Coates, W. Gerrard.

Cave, Robin John, B.A. (Oxon.). British. Worcester College, Oxford. Student. *Signed by:* L. A. K. Staveley, J. B. Leane.

Conroy, Harold, B.S. (M.I.T.), Ph.D. (Harvard). American. Brandeis University, Waltham 54, Massachusetts, U.S.A. Assistant Professor. *Signed by:* J. B. Hendrickson, J. H. Richards.

Couzens, Peter John, B.Sc. (Lond.). British. 34, Campbell Avenue, Ilford, Essex. Research Student. *Signed by:* L. J. Couzens, M. J. S. Dewar.

Cross, Alexander Dennis, B.Sc. and Ph.D. (Nott.). British. 69, Genesee Park Boulevard, Rochester 11, N.Y., U.S.A. Research Fellow of the University of Rochester. *Signed by:* D. S. Tarbell, W. Saunders.

Crump, John William, B.A. (Calif.). American. 219, Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A. Graduate Student. *Signed by:* D. Y. Curtin, R. Stolow.

Dowbenko, Rostyslaw, Ph.B. (Northwestern). American. Chemistry Department, Northwestern University, Evanston, Illinois, U.S.A. Graduate Student. *Signed by:* H. L. Dryden, F. G. Bordwell.

Duell, Michael John. British. Fairholme, Renton Drive, Guiseley, Nr. Leeds, Yorks. Student *Signed by:* A. J. B. Robertson, V. Gold.

Earl, Nicholas John. British. 23, Marion Cresent, Maidstone, Kent. Student at University College, Oxford. *Signed by:* L. A. K. Staveley, E. J. Bowen.

Edwin, Elisha Eliazer, B.A. (Madras), M.Sc. (Lond.). Indian. 103, King Charles Road, Surbiton, Surrey. Research Chemist. *Signed by:* P. Mamalis, D. McHale, B. W. Glasson.

Elliott, Keith, B.Sc. (Lond.). British. 221, Charlbury Road, Nottingham. Research Chemist. *Signed by:* C. A. Bartram, N. C. Knight.

Erskine, Richard Leslie, B.Sc. (Lond.), A.R.C.S. British. 54, Nelson Road, S. Chingford, E.4. Research Assistant at Imperial College. *Signed by:* E. S. Waight, L. M. Jackman.

Fazakerley, Harry, B.Sc. (Manc.). British. c/o 30, Latimer Road, Headington, Oxford. Research Student at Oxford University. *Signed by:* L. A. K. Staveley, D. W. Dicker.

Findlay, Stephen Powell, A.M., and Ph.D. (Princeton). American. National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda 14, Maryland, U.S.A. Research in Organic Chemistry. *Signed by:* H. G. Fletcher, E. Mosettig.

Frahn, John Leslie, M.Sc. (Adelaide), Ph.D. (Edin.). Australian. Division of Biochemistry and General Nutrition, C.S.I.R.O., Adelaide University, South Australia. Research Officer. *Signed by:* J. A. Mills, H. J. Rodda, B. O. West.

Garbers, Christoph Friedrich, M.Sc. (Pretoria), Ph.D. (Zurich). South African. National Chemical Research Laboratories, P.O. Box 395, Pretoria, South Africa. Research Chemist. *Signed by:* D. H. S. Horn, J. P. de Villiers.

Greenhalgh, Edward. British. 22, Lupin Avenue, Farnworth, Lancs. Student at Liverpool University. *Signed by:* A. Hickling, A. K. Holliday.

Hackmann, Johannes Thomas. Dutch. 2, Dence Park, Herne Bay, Kent. Senior Research Chemist at the Woodstock Agricultural Research Centre, Sittingbourne. *Signed by:* J. K. Eaton, J. Yates.

Harry, Ernest Roland. British. 183, Cathedral Road, Cardiff. Assistant Analyst to Messrs. J. Campbell Harry and Co. Ltd., Cardiff. *Signed by:* H. R. Harry, K. W. Sykes.

Hathaway, Brian John, B.Sc. (Lond.), A.R.I.C. British. 4, Western Terrace, The Park, Nottingham. Demonstrator at Nottingham University. *Signed by:* R. E. Ford, W. E. Addison.

Haynes, Charles Geoffrey, B.Sc. (Lond.). British. 107, Portal Road, Grangemouth, Stirlingshire. Research Chemist. *Signed by:* D. S. Davies, J. F. McGechen.

Herrington, Thelma Marlow. British. 35, Spencer Road, W. Wimbledon, S.W.20. Student at Oxford University. *Signed by:* L. A. K. Staveley, M. L. Tomlinson.

Howell, Walter Colston, M.Sc. and Ph.D. (Western Ontario). Canadian. 1B, Burns Street, Nottingham. Postdoctorate Fellow at Nottingham University. *Signed by:* H. Booth, C. C. Addison.

Jones, Paul Raymond, B.A. (Albion Coll.). American. 259, Noyes Laboratory, Urbana, Illinois, U.S.A. Graduate Student at the University of Illinois. *Signed by:* D. Y. Curtin, E. J. Corey.

Knowles, Aubrey. British. 24, Percy Road, Winchmore Hill, London, N.21. Student. *Signed by:* M. J. S. Dewar, W. J. Hickinbottom.

Kovacs, Odon Kalman Jozsef, Ph.D. (Szeged). Hungarian. Institute of Organic Chemistry, The University, Szeged, Beloiannisz-ter 8, Hungary. Associate Professor. *Signed by:* G. Fodor, J. Kovacs.

Lambert, Robert Wilson. British. Fold Farm, Kettlewell, Skipton, Yorks. Student at King's College, London. *Signed by:* J. Honeyman, A. J. B. Robertson.

Levin, Stephen Harris, Ph.B. and M.S. (Chicago). American. Department of Chemistry, University of Wisconsin, Madison 6, Wis., U.S.A. Student. *Signed by:* J. R. Dyer, E. E. Smissman.

Lloyd, Gordon, B.Sc. (Liv.). British. 25, Derwent Avenue, Prescot, Lancs. Research Chemist. *Signed by;* W. B. Whalley, R. J. S. Beer.

McKellar, John Ralph, B.Sc. (Adelaide). Australian. 23, Camroc Avenue, Blair Athol, Enfield, South Australia. Student. *Signed by:* B. O. West, I. S. Walker.

McNicoll, Hilary. British. 4, Apsley Street, Oakworth, Keighley, Yorks. Student. *Signed by:* D. M. Grove, R. F. Garwood.

Magee, Brigid Teresa, B.Sc. (N.U.I.). British. Glenferry, Regent Road, Altrincham, Cheshire. Teacher. *Signed by:* G. R. Barker, M. A. Parsons.

Marks, Burton S., M.S. (Miami), Ph.D. (Polytech. Inst. of Brooklyn). American. 1717, Walnut Avenue, Niagara Falls, N.Y., U.S.A. Senior Research Chemist. *Signed by:* P. E. Hoch, A. Katchman.

Masamune, Satoru, A.B. (Tohoku). Japanese. Department of Chemistry, University of California, Berkeley 4, California, U.S.A. Graduate Student. *Signed by:* A. Streitwieser, jun., J. Jiu, D. S. Noyce.

Matthews, Gerald William John. British. 10, Beresford Street, Stoke, Plymouth. Student at Nottingham University. *Signed by:* C. C. Addison, J. C. Roberts.

Mellander, Olof. Swedish. Department of Medical Biochemistry, University of Gothenburg, Sweden. Professor of Medical Biochemistry. *Signed by:* E. Stenhagen, J. Asselineau.

Middleton, John Ernest, B.Sc. (Lond.). British. 54, Malmesbury Road, South Woodford, London, E.18. Lecturer in Chemistry at Leeds College of Technology. *Signed by:* A. J. B. Spaull, W. R. Burnham.

Miller, Nicholas, B.Sc. and Ph.D. (Lond.), F.R.I.C., F.R.S.E. British. Natural Philosophy Department, The University, Edinburgh. Senior Lecturer. *Signed by:* L. J. Haynes, J. H. Knox.

O'Donnell, Thomas Aloysius, M.Sc. and Ph.D. (Melbourne). British. Chemistry Department, University of Melbourne, Carlton, N.3., Victoria, Australia. Lecturer *Signed by:* H. J. Emeléus R. N. Haszeldine.

Pantall, David Brian, B.Sc. (Nott.). British. 16, New Wanstead, London, E.11. Chemical Engineer with Messrs. A. Boake Roberts and Co. Ltd., London, E.15. *Signed by:* G. A. Weeks, J. A. Dean.

Patterson, Basil Charles. British. 18, Orchard Way, Wantage, Berks. National Serviceman. *Signed by:* G. Mattock, G. L. Davies.

Poynder, Theodore Michael, B.Sc. (Lond.). British. 31, Valentine Avenue, Bexley, Kent. Development Chemist. *Signed by:* R. G. Mason, M. F. Carroll.

Pullom, Ernest Noel, Ph.C. British. 28, Essex Street, Strand, London, W.C.2. Editor. *Signed by:* O. H. Waller, G. P. Forrester.

Read, Gordon, B.Sc. (Nott.). British. 22, Woodstock Road, Begbroke, Oxon. Research Student. *Signed by:* J. E. Davies, C. C. Addison.

Rickard, Beryl, B.Sc. (Lond.), A.R.I.C. British. Imperial College Hostel, Prince Consort Road, South Kensington, S.W.7. Demonstrator in Organic Chemistry. *Signed by:* D. R. Glasson, E. R. March.

Robinson, Ann Elisabeth, B.Pharm. (Lond.). British. 63, Pampisford Road, Purley, Surrey. Research Assistant in Pharmaceutical Chemistry. *Signed by:* A. H. Beckett, A. F. Casy.

Ryland, Thomas Owen, B.A. (Buffalo). American. P.O. Box 939, Lafayette, Indiana, U.S.A. Graduate Student at Purdue University. *Signed by:* P. Smith, H. C. Brown.

Seoane, Eliseo, Ph.D. (Madrid). Spanish. Department of Chemistry, The University, Glasgow, W.2. Chemistry Research. *Signed by:* D. H. R. Barton, P. de Mayo.

Shapiro, Elliot L., M.S. (Polytech. Inst. of Brooklyn). American. Chemical Research Department, Schering Corporation, Bloomfield, New Jersey. Research Chemist. *Signed by:* F. H. Clarke, jun., R. H. Barry.

Sharpe, Christopher James, B.Sc. (Lond.). British. 63, Nevern Square, London, S.W.5. Post Graduate research. *Signed by:* W. A. Ross, D. R. Goddard.

Sinclair, Henry Beall, B.S. (Calif.). American. Chemistry Department, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A. Student. *Signed by:* A. C. Cope, H. O. House.

Srinivasan, Parithychery Rengaswamy, M.Sc. (Banaras), Ph.D. (Madras). Indian. Department of Biochemistry, College of Physicians and Surgeons, 630W, 168th Street, New York 32, N.Y., U.S.A. Research. *Signed by:* M. P. Gordon, D. Rittenberg.

Stein, Robert A., B.S. (Northwestern), Ph.D. (Ill. Inst. of Tech.). American. Department of Physiological Chemistry, School of Medicine, University of California, Medical Center, Los Angeles 24, California, U.S.A. Research Chemist. *Signed by:* K. Mislow, D. R. Howton.

Suddaby, Olaf, B.Sc. (Dunelm). British. c/o Acheson Colloids, Ltd., Research Department, Prince Rock, Plymouth, Devon. Research Chemist. *Signed by:* E. A. Smith, R. Kellaway.

Szatkowski, Witold, B.Sc. (N.U.I.). British. 18, Manor Court Road, Hanwell, London, W.7. Research Chemist. *Signed by:* M. F. Carroll, R. L. Blackmore.

Tanner, Elsie May, B.Sc. (Lond.), A.R.I.C. British. 28, Walton Drive, Harrow, Middlesex. Physical Chemist with Parke Davies and Co. Ltd., Hounslow. *Signed by:* R. E. Bowman, E. N. Morgan.

Taylor, Kenneth John, B.Sc. (Manc.). British. 17, Weybridge House, Woodberry Down, London, N.4. Research Student. *Signed by:* G. R. Barker, W. B. Turner.

Thompson, Clifford Francis, B.S. (Maryland). American. 606, W. Ohio Street, Urbana, Illinois, U.S.A. Graduate Research Assistant, University of Illinois. *Signed by:* D. Curtin, R. J. Crawford.

Tommila, Eero Akseli, Dr.Phil. (Helsinki). Finnish. Hallituskatu 5, Helsinki, Finland. Professor of Physical Chemistry, University of Helsinki. *Signed by:* C. N. Hinshelwood, R. Nasanen.

Wells, John William, B.Sc. (Queensland). British. Chemistry Department, University of Queensland, St. Lucia, Brisbane, Queensland, Australia. Student. *Signed by:* T. G. H. Jones, I. R. Wilson.

Wilkinson, David Ian, B.Sc. (Q.U.B.). British. 104, Eglantine Avenue, Malone Road, Belfast, N. Ireland. Research Student. *Signed by:* R. G. R. Bacon, R. A. Raphael.

Wootton, Lavinia Mary Olive, B.Sc. (Bris.). British. 160, Fore Street, Hertford, Herts. Teacher. *Signed by:* W. Davey, D. H. Richardson.

Wylie, Alexander, B.Sc. (Glas.). British. 11, Clyde Road, Gourock, Renfrewshire. Research Student. *Signed by:* D. H. R. Barton, K. H. Overton.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD

Caughey, Winslow Spaulding, M.S. (New Hampshire), Ph.D. (Johns Hopkins University). American. Department of Chemistry, The Johns Hopkins University, Baltimore 18, Maryland, U.S.A. Research Chemist. *Signed by:* A. Nickon.

Hamilton, Floyd Dudley, A.B. (Emory). American. 100, Sylvia Street, West Lafayette, Indiana, U.S.A. Graduate Student at Purdue University. *Signed by:* P. Smith.

Hrutfiord, Bjorn Frederick, B.S. (Washington). American. Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, U.S.A. Student. *Signed by:* J. F. Bunnett.

Ikeda, Yoshitsugu, B.Sc. (Tokyo). Japanese. Department of Chemistry, Wakayama University, Sekido 278, Wakayama City, Japan. Assistant Professor. *Signed by:* K. Saito.

Jordan, Arthur David, jun., A.B. and M.S. (Emory). American. 304, S. Washington Avenue, Moorestown, N.J., U.S.A. Chemist with The Rohm and Haas Co. *Signed by:* D. G. Turpin.

Marker, Khursheed K. A., B.Sc. (Punjab), M.A. (Cantab.). Pakistani. Lytton Road, Quetta, Pakistan. Chemist and Director, Marker Alkaloids, Quetta. *Signed by:* H. A. Berens.

Siddiqueullah, Muhammed, M.Sc. (Dacca). Pakistani. East Regional Laboratories, Polytechnic Building, P.O. Tejgaon, Dacca, East Pakistan. Research Worker. *Signed by:* M. Q. Khuda.

Smith, Leonard, B.Sc. (Dunelm). British. 170, Wingrove Road, Fenham, Newcastle upon Tyne. National Serviceman in Malta. *Signed by:* G. A. Swan.

Stjernholm, Rune Leonard, B.S. (Stockholms Tekniska Inst.). Swedish. Western Reserve University, Medical School, Biochemistry, Cleveland, 6, Ohio, U.S.A. Graduate Student. *Signed by:* S. Pomerantz.

Stothers, John Bailie, M.Sc. (Western Ohio). Canadian. 10, Stanley Avenue, Apt. 2, Hamilton, Ontario, Canada. Graduate Student at Hamilton College, McMaster University. *Signed by:* G. S. Perry.

Wickramasinghe, A. P. Ceylonese. Clariam, Temple Road, Kalutara North, Ceylon. Assistant Master. *Signed by:* M. U. S. Sultanbawa.

PAPERS ACCEPTED

(List of Papers accepted between December 6th, 1955, and January 17th 1956, for publication in the *Journal*.)

" Cellular constituents. The chemistry of xanthine oxidase. Part II. The question of homogeneity of crystalline metallo-flavoprotein fractions." By P. G. Avis, F. Bergel, R. C. Bray, D. W. F. James, and K. V. Shooter.

" Cellular constituents. The chemistry of xanthine oxidase. Part III. Estimations of the co-factors and the catalytic activities of enzyme fractions from cow's milk." By P. G. Avis, F. Bergel, and R. C. Bray.

"The structure and reactions of dinitrogen tetroxide." By Zoltan G. Szabó, Lajos G. Bartha, and Béla Lakatos.

" Interrelationship between viscosity and boiling point of homologous liquids." By Santi R. Palit.

" The Hg–Hg bond length in the mercurous ion. Part I. The crystal structure of mercurous nitrate dihydrate." By D. Grdenić.

" The Hg–Hg bond length in mercurous ion. Part II. The crystal structure of mercurous fluoride." By D. Grdenić and C. Djordjević.

" The influence of the reaction medium on the relative apparent electron-donating effects of different alkyl groups." By E. Skinner.

" Stabilities of complex compounds of metals. Part II. The system di(tri-*n*-butylphosphine)dichloropalladium(II)-*n*-octylamine." By B. Meddings and A. R. Burkin.

" The dipole moments of pyridine, quinoline, and *iso*quinoline as vapours and as solutes." By A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif.

" Some chain-substituted methincyanines and styryl dyes." By Frances M. Hamer.

" The mechanism of the Fries rearrangement." By N. M. Cullinane, Alwyn G. Evans, and E. T. Lloyd.

" Stereochemistry of tropane alkaloids. Part IX. Selective quaternisation of tropan-3α-ol and tropan-3β-ol and of their derivatives." By Gábor Fodor, Károly Koczka, and János Lestyán.

" The reaction between cinnamic acid and phenols in presence of hydrochloric acid. A new method for the preparation of 3 : 4-dihydro-4-phenylcoumarins." By J. D. Simpson and Henry Stephen.

" Reactions of organic azides. Part V. The Schmidt reaction with fluorenones. The structure of the intermediate in the Schmidt ketonic reaction." By C. L. Arcus, M. M. Coombs, and J. V. Evans.

" Aryl-2-halogenoalkylamines. Part XVI. The preparation of derivatives of 4-[di-(2-chloroalkyl)amino]azobenzenes." By W. C. J. Ross and G. P. Warwick.

" The production of active solids by thermal decomposition. Part VIII. The calcination of calcium hydroxide." By D. R. Glasson.

" The kinetics of hydrogen isotope exchange reactions. Part V. Partial rate factors for the hydrogen isotope exchange between toluene and sulphuric acid." By V. Gold and D. P. N. Satchell.

" The preparation and stability of dialkyl chloroboronates." By M. F. Lappert.

" The polarography of niobium." By D. J. Ferrett and G. W. C. Milner.

" Thermodynamic ionization constants of barbituric acid and some of its derivatives." By A. I. Biggs.

" A new method for the preparation of 9 : 10-disubstituted anthracenes." By K. Jasper Clark.

" The synthesis and stereochemistry of some trivalent arsenic compounds." By I. G. M. Campbell and R. C. Poller.

" The preparation of *cyclo*pentenones from the products of Stobbé condensations with aliphatic ketones." By M. Elliott.

"Studies in hydrogen-bond formation. Part VI. Complex-forming properties of esters, and their relationship to the adsorption properties of cellulose acetate and other polymers." By F. M. ARSHID, C. H. GILES, and S. K. JAIN.

"The colour of organic compounds. Part IX. A comparison of isomeric dyes from 3 : 7*a*-diazaindan-1-one and -2-one." By EDWARD B. KNOTT.

"*iso*Thebaine : the synthesis of 2 : 3 : 6-trimethoxyaporphine." By K. W. BENTLEY and E. T. BLUES.

"Some observations in relation to the Reissert reaction." By R. F. COLLINS and T. HENSHALL.

"Studies on organic fluorine compounds. Part V. Infrared studies on fluoropyruvic acid and related compounds." By ERNST D. BERGMANN, ABRAHAM KALMUS, and SHRAGA PINCHAS.

"Heterocyclyl-rhodanines and -2-thiohydantoins." By EDWARD B. KNOTT.

"The hydrothermal chemistry of the silicates. Part VII. Synthetic potassium aluminosilicates." By R. M. BARRER and J. W. BAYNHAM.

"Liquid metals. Part IV. The wetting of zinc by liquid sodium; the significance of the critical wetting temperature." By C. C. ADDISON, W. E. ADDISON, D. H. KERRIDGE, and J. LEWIS.

"Cyanine dyes derived from 2-methylindolo(2' : 3-4 : 3)quinoline." By FREDERICK G. MANN and A. F. PRIOR.

"The oxidation of 2-naphthylamine with benzoyl peroxide." By S. F. D. ORR, PETER SIMS, and (in part) D. MANSON.

"The reaction between diphenylpicrylhydrazyl and 2-cyano-2-propyl radicals." By By J. C. BEVINGTON.

"Synthesis of polycyclic compounds. Part III. The formation of *as*-octahydrophenanthrene from the isomeric 2-phenylethyl*cyclo*hexanols." By (MRS.) MANJULI RAY, J. C. BARDHAN, and K. C. BHATTACHARYYA.

"Synthesis of polycyclic compounds. Part IV. Substituted 3-alkylphenanthrenes." By J. C. BARDHAN, R. N. ADHYA, and K. C. BHATTACHARYYA.

"Carcinogenic nitrogen compounds. Part XVIII. The synthesis of some polycyclic carbazoles." By HG. PH. BUU-HOÏ and PIERRE JACQUIGNON.

"Steroids and Walden inversion. Part XXX. The epimeric coprostan-3-ylamines and cholest-4-en-3-ylamines." By D. E. EVANS, H. C. RICHARDS, C. W. SHOPPEE, and G. H. R. SUMMERS.

"Solutions in sulphuric acid. Part XIX. The formation of tetra(hydrogen sulphato)-boric acid and its anion in solutions of boric acid and boric oxide." By R. FLOWERS, R. J. GILLESPIE, and J. V. OUBRIDGE.

"Chlorophyll and related substances. Part III. The synthesis of octamethylchlorin." By ULLI EISNER and R. P. LINSTEAD, with (in part) E. A. PARKES and EDITH STEPHEN.

"Homolytic aromatic substitution. Part XI. The phenylation of toluene, ethylbenzene, and *iso*propylbenzene." By D. H. HEY, B. W. PENGILLY, and GARETH H. WILLIAMS.

"Homolytic aromatic substitution. Part XII. Reactions with phenyl iodosobenzoate." By D. H. HEY, C. J. M. STIRLING, and GARETH H. WILLIAMS.

"The chemistry of extractives from hardwoods. Part XXVI. Experiments on *cyclo*eucalenol a new triterpene from *Eucalyptus microcorys*." By J. S. G. COX, F. E. KING, and T. J. KING.

"A thermodynamic study of some iodine solutions." By W. B. JEPSON and J. S. ROWLINSON.

"Photochemical changes of some deoxybenzoins." By JOSEPH KENYON, ABDEL RASSOUL, AHMED ABDEL RASSOUL, and GABRA SOLIMAN.

"The solubility of aluminium chloride in some hydrocarbons." By FRED FAIRBROTHER, NORMAN SCOTT, and HAROLD PROPHET.

"Organometallic compounds of the alkali metals. Part VI. Evidence for the formation of free alkyl radicals during certain Wurtz reactions. Homolytic reactions between alkyl-lithium compounds and alkyl halides." By D. BRYCE-SMITH.

" Nucleotides. Part XXXV. *cyclo*Pentanone oxime *p*-nitrobenzenesulphonate as an intermediate in the synthesis of nucleotide derivatives : an alternative synthesis of adenosine-5′ triphosphate." By B. H. CHASE, G. W. KENNER, SIR ALEXANDER TODD, and R. F. WEBB.

" Mechanism, kinetics, and stereochemistry of octahedral substitutions. Part IV. Bimolecular basic hydrolysis and aquation of some halogeno*iso*thiocyanatobis(ethylenediamine)cobalt(III) ions." By C. K. INGOLD, R. S. NYHOLM, and M. L. TOBE.

" Mechanism, kinetics, and stereochemistry of octahedral substitutions. Part V. Bimolecular basic hydrolysis and aquation of some halogeno- and nitrato-amminobis-(ethylenediamine)cobalt(III) ions." By R. S. NYHOLM and M. L. TOBE.

" Heterocyclic *N*-oxides. Oxides of some diphenylpyrazine derivatives and of 3-nitro- and 7-nitro-quinoline." By JUSTUS K. LANDQUIST.

" *iso*Cyano-complexes of rhodium. Part I. Tetra-*iso*cyanorhodium(I) salts." By L. MALATESTA and (MISS) L. VALLARINO.

" Structural chemistry of the alkoxides. Part V. Isomeric butoxides and amyloxides of quinquevalent tantalum." By D. C. BRADLEY, W. WARDLAW, and (MISS) A. WHITLEY.

" The conductivity of solutions in which the solvent molecule is " large." Part I. Solutions of tetraethylammonium picrate in some phthalate esters." By C. M. FRENCH and N. SINGER.

" The constitution of an oat-straw xylan." By G. O. ASPINALL and K. C. B. WILKIE.

" Conductivity studies of some thiosulphates in aqueous methanol and in aqueous ethanol." By J. R. BEVAN and C. B. MONK.

" The influence of electrolytic dissociation upon rates of reactions. Part II. The thiosulphate–propyl bromide reaction in aqueous ethanol." By J. R. BEVAN and C. B. MONK.

" The solvolysis of *n*-propyl bromide in aqueous ethanol." By J. R. BEVAN and C. B. MONK.

" Nucleophilic displacement reactions in aromatic systems. Part V. Kinetics of the reactions of some chloroazanaphthalenes and related compounds with ethoxide ions and with piperidine." By N. B. CHAPMAN and D. Q. RUSSELL-HILL.

" Kinetics of the depolymerisation of trioxan in aqueous acids, and the acidic properties of aqueous hydrogen fluoride." By R. P. BELL, K. N. BASCOMBE, and J. C. MCCOUBREY.

" The kinetics of oxidation by nitrous and nitric acid. Part III. Oxidation of oxalic acid by nitrous acid." By (MISS) P. A. VAMPLEW and K. SINGER.

" New intermediates and dyes. Part IV. Condensation of thionaphthen-2 : 3-dicarboxylic anhydride with hydrocarbons and phenols." By ARNOLD T. PETERS and DEREK WALKER.

" Organosilicon compounds. Part XVII. The acidic solvolysis of organosilicon hydrides." By J. E. BAINES and C. EABORN.

" Colombo root bitter principles. Part I. The functional groups of columbin." By D. H. R. BARTON and DOV ELAD.

" The quadrivalent fluororhenates." By R. D. PEACOCK.

" Organic reactions in sulphuric acid. Part I. Ester hydrolysis." By J. A. LEISTEN.

" Vibrational frequencies and thermodynamic properties of fluoro-, chloro-, bromo-, and iodo-benzene." By D. H. WHIFFEN.

" Ionization constants of heterocyclic substances. Part II. Hydroxy-derivatives of nitrogenous six-membered rings." By ADRIEN ALBERT and J. N. PHILLIPS.

" Raman effect of the borohydride ion in liquid ammonia solution." By L. A. WOODWARD and H. L. ROBERTS.

" A direct current integrating potentiometric circuit for the measurement of small E.M.F.s developed across high resistances." By J. I. CARASSO and R. W. PITTMAN.

" The mechanism of aromatic sulphonation and desulphonation in aqueous sulphuric acid." By V. GOLD and D. P. N. SATCHELL.

" The β-phenylserine series. Part IV." By ERNST D. BERGMANN and CH. RESNICK.

" Molecular addition compounds of dinitrogen tetroxide with nitrogen, oxygen, and aromatic hydrocarbon donors." By C. C. ADDISON and J. C. SHELDON.

" Diaryl-2 : 2'-disulphonic acids and related compounds. Part I. The diphenyl and the ditolyl series." By W. L. F. ARMAREGO and E. E. TURNER.

" Addition compounds of gallium trichloride. Part I. A comparison of the binary systems which acyl chlorides form with boron and gallium trichlorides." By N. N. GREENWOOD and K. WADE.

" Synthesis of di[*ar*-^{14}C]benzoyl peroxide from [^{14}C]benzene." By G. AYREY and C. G. MOORE.

" Esterification by sulphuric acid." By (the late) GWYN WILLIAMS and D. J. CLARKE.

" Complex Fluorides. Part V. Complexes formed by molybdenum hexafluoride, tungsten hexafluoride, and rhodium tetrafluoride." By B. COX, D. W. A. SHARP, and A. G. SHARPE.

" Stability, solvolysis, and co-ordination reactions of esters of boronic acids and their halogen derivatives." By P. B. BRINDLEY, W. GERRARD, and M. F. LAPPERT.

" Electrophilic substitution. Part II. The nitration of naphthalene and perylene." By M. J. S. DEWAR and T. MOLE.

" Nucleotides. Part XXXVI. Adenosine-2' uridine-5' phosphate." By A. M. MICHELSON, L. SZABO, and SIR ALEXANDER R. TODD.

" The solvolysis of ψ-cholesteryl toluene-*p*-sulphonate." By C. W. SHOPPEE, G. H. R. SUMMERS and R. J. W. WILLIAMS.

" Triterpenoids. Part XLVIII. Olean-13(18)-ene : isomerisation of olean-12-ene and related hydrocarbons with mineral acid." By GEORGE BROWNLIE, M. B. E. FAYEZ, F. S. SPRING, ROBERT STEVENSON, and W. S. STRACHAN.

" The occurrence of triterpenes in the Aquifoliaceae and Ericaceae of Hong Kong." By H. R. ARTHUR, C. M. LEE, and C. N. MA.

" Mesomorphism and chemical constitution. Part VII. The effect of halogen substitution on the mesomorphism of the *trans-p-n*-alkoxycinnamic acids." By G. W. GRAY, BRYNMOR JONES, and F. MARSON.

" Intermediates for the synthesis of optically active methyl-substituted long-chain acids. Part I." By R. BRETTLE and N. POLGAR.

" *peri*-Hydroxy-carbonyl compounds. Part I. The synthesis of *peri*-hydroxyindanones, tetralones, and benzo*cyclo*heptenones." By N. F. HAYES and R. H. THOMSON.

" A study of melanin formation by use of 2-(3 : 4-dihydroxy[3-^{14}C]phenyl)-, 2-(3 : 4-dihydroxy[4-^{14}C]phenyl)-, and 2-(3 : 4-dihydroxy[5-^{14}C]phenyl)ethylamine." By G. A. SWAN and D. WRIGHT.

" Oxanil." By D. BUCKLEY and H. B. HENBEST.

" Phenoxyacetic acid." By R. BRETTLE.

ADDITIONS TO THE LIBRARY

ALUMINIUM-ZENTRALE E.V. Das chemische Verhalten von Aluminium. Aluminium-Verlag. **1955.**

BARNETT, E. DE B. Mechanism of organic chemical reactions. **1956.** Blackie.
(Presented by Author.)

XIV^{e} CONGRÈS INTERNATIONAL DE CHIMIE PURE ET APPLIQUÉE. Zürich, 21—27 VII **1955.** Conférences principales et conférences de sections. **1955.** Birkhäuser.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. The investigation of atmospheric pollution : a report on observations in the 10 years ended 31st March, **1954.** 27th report. **1955.** H.M.S.O.
(Presented by D.S.I.R.)

MAYER, A., and PRICE, W. J. Chemical and spectrographic analysis of magnesium and its alloys. **1954.** Magnesium Elektron Ltd.
(Presented by Publishers.)

ORGANISATION FOR EUROPEAN ECONOMIC CO-OPERATION. Chemical Products Committee. The chemical industry in Europe. A study prepared by the Chemical Products Committee in September **1955.** **1955.** O.E.E.C. (Presented by Publishers.)

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	Dr. K. H. Pausacker, Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc, Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, Research Department, Widnes Laboratory, Widnes.
Manchester.	G. R. Barker, B.Sc., Ph.D., Chemistry Department, The University, Manchester, 13.
,,	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
Newcastle and Durham.	G. A. Swan, D.Sc., Ph.D., F.R.I.C., Department of Chemistry, King's College, Newcastle-on-Tyne, 1.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, PhD., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham.	C. C. Addison, D.Sc., Ph.D., F.R.I.C., Chemistry Department, The University, University Park, Nottingham.
Oxford.	L. A. K. Staveley, M.A., Inorganic Chemistry Laboratory, South Parks Road, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A.R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	K. W. Sykes, M.A., B.Sc., D.Phil., Department of Chemistry, University College, Singleton Park, Swansea.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING MAY, 1956

LONDON.

Thursday, May 3rd, 1956, at 7.30 p.m.

The papers presented will include:

"Transport to the surface of a rotating disc." By D. P. Gregory and A. C. Riddiford.

"The behaviour of monolayers of radio carbon tagged soap." By S. Flengas and Sir Eric Rideal.

"The preparation of active solids by thermal decomposition. Part IX. The calcination of ferric oxide hydrate and of lepidocrocite." By J. F. Goodman and S. J. Gregg.

Abstracts of the Papers for discussion may be obtained from the General Secretary.

EXETER.

Thursday, May 3rd, 1956, at 5 p.m.

Lecture, **Surface Diffusion**, by Professor R. M. Barrer, D.Sc., F.R.I.C. To be given in the Washington Singer Laboratories.

IRISH REPUBLIC.

Wednesday, May 2nd, 1956, at 7.45 p.m.

Lecture, **Seaweeds and their Utilisation**, by Dr. F. N. Woodward, B.Sc., F.R.S.E., F.R.I.C. Joint Meeting with the Institute of Chemistry of Ireland, the Royal Institute of Chemistry, and the Society of Chemical Industry, to be held in the Chemistry Department, University College, Dublin.

Thursday, May 4th, 1956, at 7.45 p.m.

Lecture, **Seaweeds and their Utilisation,** by Dr. F. N. Woodward, B.Sc., F.R.S.E., F.R.I.C. Joint Meeting with the Institute of Chemistry of Ireland, the Royal Institute of Chemistry, and the Society of Chemical Industry, to be held at University College, Cork.

Monday, May 7th, 1956, at 7.45 p.m.

Lecture, **Seaweeds and their Utilisation,** by Dr. F. N. Woodward, B.Sc., F.R.S.E., F.R.I.C. Joint Meeting with the Institute of Chemistry of Ireland, the Royal Institute of Chemistry, and the Society of Chemical Industry, to be held in the Chemistry Department, University College, Galway.

Friday, May 18th, 1956, at 7.45 p.m.

Lecture, **Applications of Infrared Spectroscopy in Chemistry,** by Dr. H. W. Thompson, M.A., F.R.S. Joint Meeting with the Werner Society to be held in the University Chemical Laboratory, Trinity College, Dublin.

NEWCASTLE AND DURHAM.

Monday, May 21st, 1956, at 5.15 p.m.

Lecture, **Steric Hindrance in Analytical Chemistry,** by Dr. H. M. N. H. Irving, M.A., D.Phil., F.R.I.C. Joint Meeting with Durham Colleges Chemical Society to be held in the Science Laboratories, The University, South Road, Durham.

OFFICIAL ANNOUNCEMENTS

DEATHS

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Horatio Ballantyne (Tadworth)	June 19th, 1892.	Jan. 25th, 1956.
Vincent Binns (Crewe)	May 6th, 1954.	Dec. 16th, 1955.
Delbert Francis Brown (Linden, N.J.)	May 1st, 1947.	Nov. 16th, 1955.
David Agnew Griffith (Par, Cornwall)	Feb. 2nd, 1888.	Jan. 12th, 1956.
Gopal Balkrishn Kolhatkar (Poona, 4)	Feb. 19th, 1914.	Nov. 9th, 1955.
William Francis Martin (Edinburgh)	Dec. 3rd, 1925.	Nov. 7th, 1955.
Gilbert George Sargeant Pullen (Whitton)	Apr. 15th, 1943.	Jan. 12th, 1956.
George Henry Purvis (Usk, Mon.)	Feb. 18th, 1926.	Dec. 26th, 1955.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows who completed 60 years of Fellowship on February 20th, 1956:

Ernest Haynes Jeffers (Chelmsford).
Thomas Francis Rutter (Braunton).

and to the following Fellows who completed 50 years of Fellowship on February 12th, 1956:

Thomas Going Stoney Bogue (Dublin).
Thomas Harold Durrans (Worcester).
Walter Hamis Glover (Box).
Henry Carlisle Irving (Dawlish).
John Parkin (Wigton).
William Hughes Perkins (St. Albans).
Percy Charles Thornton (Sidcup).
Hardolph Wasteneys (Toronto).
Henry Edgar Watt (Edinburgh).

ELECTION OF NEW FELLOWS.

The following 65 candidates were elected Fellows of the Society on February 16th, 1956:

Brian Adcock.
Anthony Leonard Andrews.
Om Prakash Agarwal.
Richard Bentham Arnold.
Roy Leonard Barnden.
Terence John Barnes.
Dieter Wolfgang Blum.
Derek David Chapman.
Jeffrey Colin Clayton.
Brian Cleaver.
Hugh Edryd Joshua Davies.
Lois Jean Durham.
Brian Colin Easton.
Frederick Gareth Robert Gimblett.
Michael Francis Harold Godwin.
Gordon Edwin Hall.
Jill Handisyde.
James Ralph Hanson.
Geoffrey Ellis Harwood.
Anna Elisabeth Hell.
Helen Margaret Higson.
Jerome Hollander.
Ralph Hollinghurst.
Gillian Iris Mary Hurdman.
Colin Jackson.
John Royston Jones.
Raymond Arthur Jones.
Aung Khin.
Takashi Kubota.
Kenneth George Mallett.
Puthamkurichi Subramanyaiyer Mayuranathan.
Alec Mee.
Laszlo Mester.
John Alfred Miller.
Laxman N. Mulay.
Masumi Nakamichi.
Raghoonandan Nery.
Albert Norton.
Raymond James Otter.
Mervyn Evan Peel.
Rodney John Perriman.
Marion Doreen Pitches.
David John Bretton Potter.
Terence Edward Rogers.
Barbara Roth.

Edward Joseph Rothery.
Adrian John Ryan.
John James Scott.
Keith Morton Seymour.
Leonard Harold Skinner.
Benjamin Sklarz.
James Dudley Spainhour.
James Bryan Stone.
Kenneth George Tapping.
James Trotter.
Jyoti Prasad Varma.
Krishnaswamy Venkaji.
Walter Anthony Vredenburgh.
Michael John Waghorn.
Derek Walker.
Rahula Oliver Barnes Wijesekera.
David Victor Wise.
John Raymond Wooldridge.
Salah Mohamed Abdel Dayem Zayed.
Maurizio Zifferero.

CORDAY-MORGAN MEDAL AND PRIZE.

The Corday-Morgan Medal and Prize for 1954 has been awarded to Dr. Rex Edward Richards.

This Award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 are due before the end of 1957.

QUARTERLY REVIEWS.

Quarterly Reviews, Vol. X, No. 1, will contain the following articles:

"The properties and nature of adsorbent carbons," by J. J. Kipling.
"Phenol tautomerism," by R. H. Thomson.
"The principles of conformational analysis," by D. H. R. Barton and R. C. Cookson.
"Radioactivation analysis," by E. N. Jenkins and A. A. Smales.
"The indole alkaloids excluding harmine and strychnine," by J. E. Saxton.

It is expected that forthcoming issues will contain the following articles:

"Silyl compounds," by A. G. MacDiarmid.
"Nuclear methylation of flavonoids," by T. R. Seshadri.
"Peptides: methods of synthesis and terminal-residue studies," by H. D. Springall and H. D. Law.

THE PHYSICAL SOCIETY EXHIBITION OF SCIENTIFIC INSTRUMENTS AND APPARATUS.

This exhibition will be held at the Royal Horticultural Society's Old and New Halls, Westminster, London, S.W.1, from May 14th to 17th, 1956. Fellows of the Chemical Society can obtain special tickets to visit the Exhibition on the Physical Society's members' morning, Monday, May 14th, when the Exhibition is not so crowded. Fellows wishing to attend the Exhibition on this day should apply for tickets to the General Secretary, The Chemical Society, Burlington House, London, W.1.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at the Royal Institution, Albemarle Street, London, W.1, on Thursday, February 2nd, 1956, at 2.30 p.m.

The President, Professor W. Wardlaw, C.B.E., D.Sc., F.R.I.C., was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at the Imperial College of Science and Technology on January 19th, 1956, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: D. J. Morley, A. Barker, Henry Rapoport, Leslie C. Johnson, K. Reynolds, D. J. Fry, D. G. Wilkinson.

SYMPOSIUM.

The President called upon Dr. R. P. Linstead, C.B.E., F.R.S., to take the Chair for the afternoon session of the Symposium entitled "Recent Advances in the Chemistry of Colouring Matters." The following contributions were made and discussed:

1. "Steric Effects in Azo and Indigoid Dyes." By Wallace R. Brode (Washington).
2. "*cis–trans*-Isomerism in Azo-dyestuffs." By R. H. Peters and E. Atherton (Manchester).
3. "Synthesis of Azaporphins and Related Macrocycles." By J. A. Elvidge (Imperial College).

The meeting then adjourned, and in the evening the Chair was taken by Sir Alexander Todd, F.R.S. The following papers were read and discussed:

1. "Synthetic Carotenoids." By O. Isler, H. Lindlar, M. Montavon, R. Ruegg, G. Saucy, and P. Zeller (Basle). Dr. Isler read the paper.
2. "Modern Theories of Colour." By M. J. S. Dewar (London).

At the close of the discussion, the Chairman expressed the thanks of the Society to the contributors to the Symposium.

Minutes of a

SCIENTIFIC MEETING

held in the Large Chemistry Theatre of the University of Manchester on Thursday, February 9th, 1956, at 6.30 p.m.

The President, Professor W. Wardlaw, C.B.E., D.Sc., F.R.I.C., was in the Chair.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: J. A. D. Ewart, Neville H. P. Smith, J. A. Schofield, Herbert Buchwald, G. H. Foxley, J. A. Farrington, W. F. Hodson, M. Thompson, Brian R. Smith, Alan Taylor, Teresa Magee.

TILDEN LECTURE.

The President called upon Dr. G. W. Kenner to deliver the Tilden Lecture entitled "Recent Progress in the Chemistry of Peptides." At the conclusion of the Lecture, a vote of thanks to Dr. Kenner, proposed by Professor A. J. Birch, was carried with acclamation.

Minutes of a

SCIENTIFIC MEETING

held at Burlington House, on Thursday, February 16th, 1956, at 7.30 p.m.

Sir Alexander Todd, M.A., D.Sc., F.R.S., Vice-President, was in the Chair.

MINUTES.

The Minutes of the Scientific Meetings held at the Royal Institution and at the University of Manchester, on February 2nd and 9th, respectively, were read, and were confirmed and signed.

VACANCIES ON COUNCIL, 1956–57.

The list of nominations was read.

APPOINTMENT OF SCRUTATORS.

Mr. P. F. G. Praill and Dr. W. C. J. Ross were appointed scrutators for the ballot for the election of Vice-President and Ordinary Members of Council.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: F. Bergel, J. H. Pryor, G. W. Kenner, B. D. Owen, I. R. Wilson, G. P. Warwick, J. J. Roberts, Walter Davis, R. C. Bray, E. W. Crunden, C. A. Vernon.

SCIENTIFIC COMMUNICATIONS.

The following papers were read and discussed:

"Aryl-2-halogenoalkylamines. Part XVIII. The Rates of Reduction of Substituted 4-(Di-2-chloroethylamino)azobenzenes by Stannous Chloride, Hydrazine, and the Xanthine Oxidase–Xanthine System." By W. C. J. Ross and G. P. Warwick.

"A New and Specific Aromatisation Reaction." By P. A. Robins and James Walker.

"Mechanisms of Hydrolysis of Organic Phosphates. Parts I and II." By C. A. Bunton, D. R. Llewellyn, K. G. Oldham, and C. A. Vernon.

PAPERS ACCEPTED

(List of Papers accepted between January 19th and February 17th, 1956, for publication in the *Journal*.)

"The selective absorption of optical antipodes by proteins. Part III." By William Bradley and Richard A. Brindley.

"Glycine peptides. Part II. The heat and entropy of formation of the peptide bond in polyglycine." By A. B. Meggy.

"Thermochemistry of organophosphorus compounds. Part II. Triethyl phosphate, tripropylphosphine oxide, and tributylphosphine oxide." By C. L. Chernick and H. A. Skinner.

"Bridged complexes of palladium(II) containing chelate ligands." By S. E. Livingstone.

"Bridged complexes of platinum(II) containing chelate groups." By S. E. Livingstone.

"The lowest singlet excited levels of naphthalene. Part I. A semi-empirical calculation." By R. Lefebvre and C. Moser.

"The chemistry of the transition elements. Part I. Dimeric carbonyl complexes of platinum." By R. J. Irving and E. A. Magnusson.

" Interdependence of molecular conformation and conjugation in aromatic ethers. Part I." By G. BADDELEY, N. H. P. SMITH, and M. A. VICKARS.

" Correlation between reactivity of the 1-carbon atom in alcohols, and certain properties of alkoxylsilanes." By W. GERRARD and K. D. KILBURN.

" A study of the Stephen reaction." By L. TURNER.

" Solid–liquid equilibria in solutions of non-electrolytes." By R. P. RASTOGI and K. T. RAMA VARMA.

" Adsorption of complex anions from uranyl sulphate solution by anion-exchange resins." By T. V. ARDEN and G. A. WOOD.

" Electrometric titration of the sodium salts of deoxyribonucleic acids. Part III. The effect of sodium chloride." By R. A. COX and A. R. PEACOCKE.

" Synthesis of polycyclic compounds. Part V. The cyclodehydration of 3-benzyl-*cyclo*hexanol." By J. C. BARDHAN and R. C. BANERJEE.

" Reactions of organic azides. Part VI. The interaction of 2-acylbenzoic acids and alkylidenephthalides with hydrazoic and sulphuric acids." By C. L. ARCUS and R. E. MARKS.

" Secondary mechanisms in the halogenation of phenols and aromatic sulphonamides." By P. W. ROBERTSON.

" Cyclic sulphites derived from the chloropropanediols." By P. B. D. DE LA MARE, W. KLYNE, D. J. MILLEN, J. G. PRITCHARD, and D. WATSON.

" Synthesis of 10-methyl-3 : 4-benzopyrene and 8 : 10-dimethyl-3 : 4-benzopyrene." By A. D. CAMPBELL.

" The preparation of nitrosoalkanes from alkyl nitrites." By B. G. GOWENLOCK and J. TROTMAN.

" The determination of small concentrations of alcohols." By V. S. GRIFFITHS and D. I. STOCK.

" Halogenation in acid solution. The formation of iodoform from malonic acid." By M. G. BROWN.

" Aryl-2-halogenoalkylamines. Part XVII. The ultraviolet absorption spectra of some 4-(di-2-chloroethylamino)azobenzenes in neutral and acidic ethanol solutions." By W. C. J. ROSS and G. P. WARWICK.

" Aryl-2-halogenoalkylamines. Part XVIII. The rates of reduction of substituted 4-(di-2-chloroethylamino)azobenzenes by stannous chloride, hydrazine, and the xanthine oxidase–xanthine system." By W. C. J. ROSS and G. P. WARWICK.

" The structure of sterculic acid." By P. K. FAURE and J. C. SMITH.

" Quantitative aspects of the base-catalysed halogenation of aliphatic ketones. Part I. Iodination of methyl ketones." By C. F. CULLIS and M. H. HASHMI.

" Fatty acids. Part IV. The preparation of eight 9 : 10 : 12 : 13-tetrahydroxystearic acids." By K. E. BHARUCHA and F. D. GUNSTONE.

" The atom polarisations of some co-ordination compounds of metals." By (MRS.) J. MACQUEEN and J. W. SMITH.

" An alkaloid of *Dioscorea hispida*, Dennstedt. Part III. Further investigations on the Hofmann degradation." By A. R. PINDER.

" A simple approximation to the resonance energies of aromatic molecules." By A. L. GREEN.

" The possible existence of transition-metal complexes of *cyclo*butadiene." By H. C. LONGUET-HIGGINS and L. E. ORGEL.

" The behaviour of ion-exchange resins with mixed solvents." By C. W. DAVIES and B. D. R. OWEN.

" The adsorption of organic acid molecules and their chromatographic separation on ion-exchange resins." By C. W. DAVIES and B. D. R. OWEN.

" The oxidative degradation of sterculic acid." By J. P. VERMA, BHOLA NATH, and J. S. AGGARWAL.

" Synthesis of leprapinic acid and constitution of pinastric acid." By O. P. MITTAL and T. R. SESHADRI.

"1 : 2-3 : 4-8 : 9-10 : 11-Tetrabenzopentacene." By E. CLAR, W. KELLY, and W. G. NIVEN.

"Antimalarial studies in the pteridine field." By M. D. POTTER and T. HENSHALL.

"The structure and mechanism of formation of the polymer obtained from *cyclo*propane by mercury photosensitisation." By K. J. IVIN.

"Triterpenoids. Part XXII. The constitution and stereochemistry of masticadienonic acid." By D. H. R. BARTON and E. SEOANE.

"Oxidation of dialkyl sulphides and trisubstituted phosphines by dinitrogen tetroxide; molecular addition compounds with dialkyl sulphoxides." By C. C. ADDISON and J. C. SHELDON.

"The components of wool wax. Part III. 7-Oxocholesterol and the alleged presence of cholestanol." By A. H. MILBURN and E. V. TRUTER.

"The components of wool wax. Part IV. The identification of some steroidal derivatives." By A. H. MILBURN, E. V. TRUTER, and F. P. WOODFORD.

"The dinitration of *p*-di-*tert.*-butylbenzene." By F. BELL and K. R. BUCK.

"The reactivity of the *O*-acylglycosyl halides. Part IV. The solvolytic reactions of *O*-acetyl-α-D-glycosyl 1-halides in the presence of electrophilic catalysts." By G. L. MATTOK and G. O. PHILLIPS.

"Complex fluorides. Part VI. The properties of silver salts of fluoro-acids and their interaction with aromatic hydrocarbons." By D. W. A. SHARP and A. G. SHARPE.

"Potential radiosensitizers: some quinones and related compounds." By K. J. M. ANDREWS, D. H. MARRIAN and D. R. MAXWELL.

"The synthesis of 2-deoxy-2-fluorotetritols and 2-deoxy-2-fluoro-(±)-glyceraldehyde." By N. F. TAYLOR and P. W. KENT.

"Aluminium tri-soaps." By A. GILMOUR, A. JOBLING, and S. M. NELSON.

"The preparation of [^{14}C]dimethylamine and [^{14}C]dimethylnitrosamine." By MRS. A. H. DUTTON and D. F. HEATH.

"Thiazoles derived from chrysean and *iso*chrysean." By A. ADAMS and R. SLACK.

"Purines, pyrimidines, and glyoxalines. Part II. New syntheses of some pyrimidine nucleosides." By R. K. RALPH and G. SHAW.

"Triterpenoids. Part XLIX. The constitution of the ester $C_{33}H_{46}O_7$ obtained by oxidation of methyl glycyrrhetate acetate." By GEORGE BROWNLIE and F. S. SPRING.

"Quaternary ammonium nitrates. Part II. Reactions of nitratoalkyl ethers, amines, amides, and urethanes with tertiary amines and related compounds." By E. S. LANE.

"Triterpenoids. Part XXIII. The nature of lantadene A." By D. H. R. BARTON, P. DE MAYO, and J. C. ORR.

"Complex fluorides. Part VII. Cuprous salts of fluoro-acids and aromatic hydrocarbons." By D. W. A. SHARP and A. G. SHARPE.

"Further studies in the dihydroxynaphthalenes." By NG. PH. BUU-HOÏ and DENISE LAVIT.

"Methylnicotinic acids. Part I. Condensation of 2-methyl-6-phenylnicotinic acid and its ethyl ester with aldehydes." By E. TITTENSOR and D. G. WIBBERLEY.

"Condensation products of phenols and ketones. Part X. The structure of Dianin's compound, a unique inclusion-forming substance." By WILSON BAKER, A. J. FLOYD, J. F. W. MCOMIE, G. POPE, A. S. WEAVING, and J. H. WILD.

"Condensation products of phenols and ketones. Part XI. A rational synthesis of Dianin's compound." By WILSON BAKER, J. F. W. MCOMIE, and A. S. WEAVING.

"Stereochemistry of tervalent arsenic compounds. Part II. Optical resolution of 2-*p*-carboxyphenyl-5-methyl-1 : 3-dithia-2-arsaindane." By I. G. M. CAMPBELL.

"Organometallic and organometalloid compounds. Part I. Silicon derivatives of 2-amino-1 : 3-diphenylcrotononitrile." By R. A. SHAW.

"Triterpenoid constituents of *Siphonodon australe* Benth. Part I. Ketones of the friedelane series." By J. L. COURTNEY and R. M. GASCOIGNE.

"Triterpenoid constituents of *Siphonodon australe* Benth. Part II. Hydroxyketones and alcohols of the friedelane series." By J. L. COURTNEY, R. M. GASCOIGNE, and A. Z. SZUMER.

"7-Nitro-1-naphthylamine. Part I. Its preparation, halogenation, and diazo-coupling; and 1 : 2 : 4 : 7-tetrahalogenonaphthalenes." By A. HARDY, E. R. WARD, and (in part) L. A. DAY.

"The tropylium ion. Part I. Synthesis of tropylium and methyltropylium salts." By M. J. S. DEWAR and R. PETTIT.

"The tropylium ion. Part II. A further synthesis and some reactions of tropylium salts." By M. J. S. DEWAR and R. PETTIT.

"Triterpenoids. Part L. The constitution of butyrospermol." By D. S. IRVINE, WILLIAM LAWRIE, A. S. MCNAB, and F. S. SPRING.

"Oxazolopyridines and oxazoloquinolines. Part I. 2'-Alkyl- and 2'-aryl derivatives of oxazolo(4' : 5'-3 : 4)pyridine and oxazolo(4' : 5'-3 : 4)quinoline." By JAMES FRASER and E. TITTENSOR.

"Some heterocyclic quaternary dichloroiodides." By FRANCES M. HAMER.

"An anomalous reaction of 4 : 6-dichloro-5-nitropyrimidine." By F. L. ROSE and D. J. BROWN.

"The synthesis of some indolylalkylamines." By D. E. AMES, R. E. BOWMAN, D. D. EVANS, and W. A. JONES.

"Steroids and Walden inversion. Part XXXIII. The configurations of the coprostanyl halides." By R. J. BRIDGWATER, D. N. JONES, C. W. SHOPPEE, and G. H. R. SUMMERS.

ADDITIONS TO THE LIBRARY

BACKER, H. J. Oude chemische wertuigen en laboratoria van Zosimos tot Boerhaave. J. B. Wolters. 1955.
(Presented by the Author.)

BACON, G. E. Neutron diffraction. O.U.P. 1955.

BORESKOV, G. K. Catalysis in the sulphuric acid industry. (In Russian.) 1954.
(Presented by the Academy of Sciences of the U.S.S.R.)

CADLE, R. D. Particle size determination. Interscience. 1955.

CHRISTOFFEL, C. Über Acylderivate von Aminosäuren. Orell Füssli. 1946.
(Presented by Messrs. L. Light and Company Ltd.)

COLE, S. W. Cole's practical physiological chemistry, 10th ed. Revised and re-written by E. Baldwin and D. J. Bell. W. Heffer and Sons. 1955.
(Presented by Dr. D. J. Bell.)

DENBIGH, K. The principles of chemical equilibrium, with applications in chemistry and chemical engineering. C.U.P. 1955.

DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH. A brief review of science and technology in Western Germany. H.M.S.O. 1955. (Presented by D.S.I.R.)

DERYAGIN, B. V., and KROTOVA, N. A. Adhesion. (In Russian.) 1949.
(Presented by the Academy of Sciences of the U.S.S.R.)

FRANK-KAMENETSKII, D. A. Diffusion and heat exchange in chemical kinetics. (Translated by N. Thon.) Princeton University Press. 1955.

FRIEDLANDER, G., and KENNEDY, J. W. Nuclear and radiochemistry. Wiley. 1955.

GURNHAM, C. F. Principles of industrial waste treatment. Wiley. 1955.

HILGER AND WATTS LTD. The analysis of aluminium and its alloys with the direct reading attachment to the medium spectrograph. Hilger and Watts Ltd. 1955.
(Presented by the Publishers.)

INGRAM, D. J. E. Spectroscopy at radio and microwave frequencies. Butterworths. 1955.

INTERNATIONAL COMMISSION FOR UNIFORM METHODS OF SUGAR ANALYSIS. Report of the proceedings of the 11th session, held . . . Paris . . . 1954. ICUMSA. 1956.
(Presented by the Publisher.)

JENSEN, E. H. A study on sodium borohydride, with special reference to its analytical application in organic chemistry. Arnold Busck. 1954.

KITAĬGORODSKIĬ, A. I. Organic crystallochemistry. (In Russian.) 1955.
(Presented by the Academy of Sciences of the U.S.S.R.)

LOCHTE, H. L., and LITTMANN, E. R. The petroleum acids and bases. Chemical Publishing Co. 1955.

MCQUILLAN, A. D., and MCQUILLAN, M. K. Titanium. (Metallurgy of the rarer metals, No. 4.) Butterworths. 1956.

METCALF, R. L. Organic insecticides: their chemistry and mode of action. Interscience. 1955.

MILES, F. D. A history of research in the Nobel Division of I.C.I. Imperial Chemical Industries Ltd., Nobel Division. 1955.

NESMYANOV, An. N., LAPITSKIĬ, A. V., and RUDENKO, N. P. Preparation of radioactive isotopes. (In Russian.) 1954.
(Presented by the Academy of Sciences of the U.S.S.R.)

N.V. KONINKLIJKE NEDERLANDSCHE SPRINGSTOFFENFABRIEKEN. The nitration and the denitration of cellulose nitrates. II. *X*-ray investigation. By J. Trommel. 1955.
(Presented by the Publisher.)

N.V. KONINKLIJKE NEDERLANDSCHE SPRINGSTOFFENFABRIEKEN. The nitration and the denitration of cellulose nitrates. I. By G. de Bruin and C. H. D. Witte. 1955.
(Presented by the Publisher.)

ORGANIZATION FOR EUROPEAN ECONOMIC CO-OPERATION. European Productivity Agency. Function and training of the chemical engineer: international conference held in London from 21st to 23rd March, 1955. O.E.E.C. 1955. (Presented by the Publishers.)

OSBORN, G. H. Synthetic ion-exchangers. Chapman and Hall. 1955.

PAULI, W., ROSENFELD, L., and WEISSKOPF, V. (Eds.). Niels Bohr and the development of physics: essays dedicated to Niels Bohr on the occasion of his seventieth birthday. Pergamon Press. 1955.

Progress in biophysics and biophysical chemistry. Vol. 6. Edited by J. A. V. Butler. Pergamon Press. 1956. (Presented by Professor J. A. V. Butler.)

REMY, H. Treatise on inorganic chemistry. Translated by J. A. Anderson. Edited by J. Kleinberg. Vol. 1. Introduction and main groups of the Periodic Table. Elsevier. 1956.

ROGOVIN, Z. A., and SHORYGINA, N. N. Chemistry of cellulose and its admixtures. (In Russian.) 1953.
(Presented by the Academy of Sciences of the U.S.S.R.)

SCHOELLER, W. R., and POWELL, A. R. The analysis of minerals and ores of the rarer elements. 3rd ed., revised by A. R. Powell. Griffin. 1955.

SHEDLOVSKY, T. (Ed.). Electrochemistry in biology and medicine. Wiley. 1955.

SZÖNYI, G. I. Ueber Anhydride von Aminosäuren. II. Versuch der Synthese von optisch aktiven Hydraziden. H. Hasch. 1944.
(Presented by Messrs. L. Light and Company, Ltd.)

UNITED STATES ATOMIC ENERGY COMMISSION. Chemical processing and equipment. McGraw-Hill. 1955.

U.S. DEPARTMENT OF COMMERCE. National Bureau of Standards. Circular 564. Tables of thermal properties of gases. U.S. Govt. Printing Office. 1955.
(Presented by the Bureau of Standards.)

U.S.S.R. ACADEMY OF SCIENCES. Session of the Academy on peaceful uses of atomic energy, July, 1955. Vol. 1. Chemistry division. Vol. 2. Physics and mathematics division. Vol. 3. Technical division. Vol. 4. Biology division. Vol. 5. Plenary meeting. (In Russian, with English summaries.) 1955.
(Presented by the Academy.)

VAN RYSSELBERGHE, P. Electrochemical affinity: studies in electrochemical thermodynamics and kinetics. Hermann. 1955.
(Presented by the Author.)

WALLIS, T. E. Textbook of pharmacognosy, 3rd ed. Churchill. 1955.
(Presented by the Author.)

WHITE, D. W., JUN., and BURKE, J. E. (Eds.). The metal beryllium. American Society for Metals. 1955.

WILSON, E. B., JUN., DECIUS, J. C., and CROSS, P. C. Molecular vibrations: the theory of infrared and Raman vibrational spectra. McGraw-Hill. 1955.

ZIMMERMAN, O. P., and LAVINE, I. Chemical engineering laboratory equipment. 2nd ed. Industrial Research Service, Inc. 1955.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	Dr. K. H. Pausacker, Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc, Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	G. R. Barker, B.Sc., Ph.D., Chemistry Department, The University, Manchester, 13.
,,	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
Newcastle and Durham.	G. A. Swan, D.Sc., Ph.D., F.R.I.C., Department of Chemistry, King's College, Newcastle-on-Tyne, 1.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, PhD., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham.	C. C. Addison, D.Sc., Ph.D., F.R.I.C., Chemistry Department, The University, University Park, Nottingham.
Oxford.	L. A. K. Staveley, M.A., Inorganic Chemistry Laboratory, South Parks Road, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A.R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	K. W. Sykes, M.A., B.Sc., D.Phil., Department of Chemistry, University College, Singleton Park, Swansea.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING JUNE, 1956

LONDON.

Thursday, June 7th, 1956, at 7.30 p.m.

Centenary Lecture, **Present Status of the Transuranium Elements,** by Professor G. T. Seaborg. To be held at Burlington House.

LIVERPOOL.

Tuesday, June 5th, 1956, at 5.30 p.m.

Centenary Lecture, **The Transuranium Elements,** by Professor G. T. Seaborg. Joint meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, the British Association of Chemists, and the University Chemical Society, to be held in the Chemistry Lecture Theatre of The University.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Harold King (West Parley) (C. 1928—31)	Dec. 7th, 1911.	Feb. 20th, 1956.
James Cruickshank Smith (Chester)	June 17th, 1903.	Feb. 2nd, 1956.
James King Steel (Paisley)	Feb. 16th, 1933.	Feb. 18th, 1956.
John Reginald Harvey Whiston (Swindon)	Feb. 20th, 1941.	Feb. 28th, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows who were elected to the Fellowship of the Royal Society on March 15th, 1956:

Richard Maling Barrer (London).
John Alfred Valentine Butler (London).
Charles William Shoppee (Swansea).

The President has also conveyed the congratulations of the Society to Mr. Brougham Young (London), who completed 70 years of Fellowship on March 4th, 1956.

ELECTION OF NEW FELLOWS.

The following 84 candidates were elected Fellows of the Society on March 15th, 1956:

Edward McIntosh Acton.
Krishna Sastri Aghoramurthy.
Robert Leo Augustine.
Brian Charles Baldwin.
James Edmund Banfield.
Michael Barber.
Lindsay Michael Birt.
Edward George Brain.
John Theodore Braunholtz.
Eric Bullock.
Joseph Anthony Cade.
Winslow Spaulding Caughey.
Robin John Cave.
Harold Conroy.
Peter John Couzens.
Alexander Dennis Cross.
John William Crump.
Rostyslaw Dowbenko.
Michael John Duell.
Nicholas John Earl.
Elisha Eliazer Edwin.
Keith Elliott.
Richard Leslie Erskine.
Harry Fazakerley.
Stephen Powell Findlay.
John Leslie Frahn.
Christopher Friedrich Garbers.
Edward Greenhalgh.
Johannes Thomas Hackmann.
Floyd Dudley Hamilton.
Ernest Roland Harry.
Brian John Hathaway.
Charles Geoffrey Haynes.
Thelma Marlow Herrington.
Walter Colston Howell.
Bjorn Frederick Hrutfiord.
Yoshitsugu Ikeda.
Paul Raymond Jones.
Arthur David Jordan, jun.
Aubrey Knowles.
Odon Kalman Jozsef Kovacs.
Robert Wilson Lambert.
Stephen Harris Levin.
Gordon Lloyd.
John Ralph McKellar.
Hilary McNicoll.
Brigid Teresa Magee.
Khursheed K. A. Marker.
Burton S. Marks.
Satoru Masamune.
Gerald William John Matthews.
Olof Mellander.
John Ernest Middleton.
Nicholas Miller.
Thomas Aloysius O'Donnell.
David Brian Pantall.
Basil Charles Patterson.
Theodore Michael Poynder.
Ernest Noel Pullom.
Gordon Read.
Beryl Rickard.
Ann Elisabeth Robinson.
Thomas Owen Ryland.
Eliseo Seoane.
Elliot L. Shapiro.
Christopher James Sharpe.
Muhammed Siddiqueullah.
Henry Beall Sinclair.
Leonard Smith.
Parithychery Rengaswamy Srinivasan.
Robert A. Stein.
Rune Leonard Stjernholm.
John Bailie Stothers.
Olaf Suddaby.
Witold Szatkowski.
Elsie May Tanner.
Kenneth John Taylor.
Clifford Francis Thompson.
Eero Akseli Tommila.
John William Wells.
Albert Peeris Wickramasingha.
David Ian Wilkinson.
Lavinia Mary Olive Wootton.
Alexander Wylie.

ELECTIONS TO COUNCIL, 1956–57.

At the Annual General Meeting held on March 27th, 1956, at the University of Nottingham, the election of the following to vacancies on the Council for 1956—57 was announced:

President.

Professor E. L. Hirst.

Honorary Secretary.

Dr. J. Chatt.

Vice-Presidents who have not filled of the Office of President.

Professor E. D. Hughes.

Elected Ordinary Members of Council:

Constituency I (South-East England).

Professor R. M. Barrer.
Dr. G. W. Kenner.
Dr. A. Maccoll.
Mr. L. A. K. Staveley.

Constituency II (Central and South-West England and South Wales).

Professor A. G. Evans.

Constituency IV (North-East England).

Professor L. Hunter.
Professor B. Lythgoe.

LOCAL REPRESENTATIVES.

The following appointments have been made:

Manchester: Dr. H. B. Henbest in place of Dr. G. R. Barker.

Newcastle and Durham: Dr. F. J. McQuillin and Dr. G. Kohnstam to act jointly in place of Dr. G. A. Swan.

South Wales: Dr. A. R. Pinder and Mr. R. H. Davies to act jointly in place of Dr. K. W. Sykes.

The President has conveyed the thanks of the Council to the retiring Local Representatives for their services to the Society.

SYMPOSIUM ON CHEMISORPTION.

A Symposium on Chemisorption will be held from July 17th to 19th at the University College of North Staffordshire, Keele, Staffs. Accommodation will be available in the University College for Fellows attending the meeting from the evening of Monday, July 16th, until after lunch on Thursday, July 19th, at an approximate cost of £3 15s. per person.

The complete list of contributors is not yet available, but it has been arranged that the Symposium will consist of five sessions with time for formal and informal discussions. The following have consented to act as Chairmen of the various sessions: Theory—Professor W. E. Garner, C.B.E., F.R.S.; Metals—Professor D. D. Eley; Semi-conductors—Dr. F. S. Stone; Carbon—Professor W. F. K. Wynne-Jones; and Insulators—Mr. D. A. Dowden.

Plans for publication of the Symposium are under discussion and full details of the arrangements, together with forms of application, will be sent to Fellows as soon as they can be made available.

LIBRARY—WHITSUN HOLIDAY.

The Library will be closed for the Whitsun holiday on Monday and Tuesday, May 21st and 22nd, 1956.

SECOND WORLD METALLURGICAL CONGRESS.

Fellows of the Society are invited to take part in the Second World Metallurgical Congress to be held in Chicago, Illinois, from November 2nd to 8th, 1957. Details of the Congress can be obtained from Mr. W. H. Eisenman, Secretary, American Society for Metals, 7301 Euclid Avenue, Cleveland 3, Ohio, U.S.A.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretary within ten days of the date of publication of the Journal *for April, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Abbey, Frank, B.A. (Cantab.). British. 48, Spencer Avenue, Earlsdon, Coventry, Warwicks. Research Chemist with Courtaulds, Ltd. *Signed by:* A. Rutherford, A. V. Parke.

Arndt, Reinhard Richard, B.Sc. (S. Africa), M.Sc. (Orange Free State). South African. N.C.R.L., P.O. Box 395, Pretoria, South Africa. Research Assistant. *Signed by:* D. Ilse, D. H. S. Horn.

Arris, John, B.Sc. (Dunelm). British. 14, Jesmond Park West, Newcastle upon Tyne, 7. Research Student at King's College, Newcastle upon Tyne. *Signed by:* J. G. Buchanan, J. Baddiley.

Aubrey, Derek Wilfred, B.Sc. (Sheffield). British. 9, Kenerne Drive, Barnet, Herts. Research Chemist with Adhesive Tapes, Ltd., Borehamwood. *Signed by:* P. L. Williams, G. A. Dawe.

Baines, Neville John. British. 90, Lord Street, Fleetwood. Student at Sheffield University. *Signed by:* H. J. V. Tyrrell, A. H. Lamberton.

Baum, George, B.S. (Case Inst. of Tech.). American. 4532, Far Hills Avenue, Apt. 3, Dayton 9, Ohio, U.S.A. Chemist with Wright Air Development Center, Ohio. *Signed by:* H. D. C. Hill, H. Rosenberg.

Bean, Neville Ernest. British. 28, Blackfriars Road, Gt. Yarmouth, Norfolk. Student at Oxford University. *Signed by:* H. Irving, R. E. Richards.

Beard, Colin Charles, B.Sc. (Lond.). British. 49 Abbotsford Avenue, West Green, London, N.15. Research Student at Queen Mary College, London. *Signed by:* W. J. Hickinbottom, M. S. Grant.

Beaton, John Moody, B.Sc. and Ph.D. (Glas.). British. c/o 86, Seedhill Road, Paisley, Renfrewshire. Research Assistant at The Royal Technical College, Glasgow. *Signed by:* F. S. Spring, R. Stevenson.

Biggs, John, B.A. (Cantab.). British. Downing College, Cambridge. Research Student. *Signed by:* G. W. Kirby, R. Bonnett.

Bjerrum, Jannik, Dr.Phil. (Copenhagen). Danish. Kemisk Laboratorium A, Danmarks tekniske Hojskole, Solvgade 83, Kobenhavn K, Denmark. Professor of Chemistry. *Signed by:* S. Veibel, G. Ostrup.

Brooks, Jean Winifred, B.Sc. (Lond.). British. 4, The Mead, Nazeing New Road, Broxbourne, Herts. Research Student. *Signed by:* M. M. Harris, D. M. Hall.

Brown, Anne Frances. British. 5, East Terrace, Budleigh Salterton, E. Devon. Student at Nottingham University. *Signed by:* C. C. Addison, H. Booth.

Brown, Frank, B.Sc. (Dunelm). British. 111, Durham Road, Stockton-on-Tees. Industrial Chemist. *Signed by:* T. N. Bell, D. Wright.

Brown, Patricia Margaret, B.Sc. (Aberd.). British. 3, Bath Road, Bedford Park, London, W.4. Research Student. *Signed by:* E. A. Braude, M. Whalley.

Brown, Stanley Sidney, B.Sc. (Lond.). British. 186, Camberwell Road, London, S.E.5. Research Student at Queen Mary College, London. *Signed by:* M. F. Ansell, R. F. Hudson.

Bujwid, Zdzislaw Jan, B.Sc. (Lond.). Polish. 18, Ribblesdale Road, London, N.8. Postgraduate Research Student. *Signed by:* W. Gerrard, J. A. Elan.

Bunfield, Leslie, B.Sc. (Sheffield). British. King Edward VI Grammar School, Stourbridge, Worcs. Chemistry Master. *Signed by:* S. J. Featherston, P. H. Carter.

Cantlon, Ian James. Irish. 28, Trinity College, Dublin. Student. *Signed by:* W. Cocker, T. B. H. McMurry.

Carson, James Frederick. Irish. 4, Airfield Road, Rathgar, Dublin, Eire. Student at Trinity College, Dublin. *Signed by:* W. Cocker, T. B. H. McMurry.

Case, John Reginald. British. 10, Cheyne Gardens, Liverpool 19, Student at New College, Oxford. *Signed by:* L. A. K. Staveley, A. S. Bailey.

Chaplin, Anne Elizabeth Marie, B.Sc. (Lond.). British. 2, Pretoria Road, Streatham, S.W.16. Technical Assistant with British Celanese. *Signed by:* M. H. Randall, R. Fisher.

Clarke, John Shipley, B.A. and B.Sc. (Oxon.). British. 94, Waterloo Road, Bramhall, Stockport, Cheshire. Student Teacher. *Signed by:* H. Irving, C. S. G. Phillips.

Clarkson, Richard, B.Sc. (Manc.). British. 37, Chapel Street, Barnoldswick, Colne, Lancs. Research Student. *Signed by:* L. A. K. Staveley, H. Smith.

Cogliano, Joseph A., B.S. (Brooklyn). American. Graduate College, Princeton University, Princeton, N.J., U.S.A. Graduate Student. *Signed by:* E. C. Taylor, jun., R. K. Hill.

Corpe, Thomas William, B.Sc. (Lond.). British. 88, Aldborough Road, Seven Kings, Ilford, Essex. Development Chemist. *Signed by:* G. A. Weeks, R. G. Mason.

Cross, Kenneth Nelson, A.R.I.C. British. 54, Highgate West Hill, Highgate Village, London, N.6. Research Chemist with Messrs. Carreras, Ltd., London, N.W.1. *Signed by:* E. de B. Barnett, R. F. Branch.

Dawkins, Arthur William, B.Sc. (Lond.). British. 62, Carve Ley, Welwyn Garden City, Herts. Organic Research Chemist. *Signed by:* J. F. Grove, T. P. C. Mulholland.

Dietrich, Henri, Dr.sc.nat. (E.T.H., Zurich). Swiss. 46, Buckingham Avenue, Feltham, Middlesex. Research Chemist with Messrs. Parke-Davis & Co., Hounslow. *Signed by:* A. Campbell, E. N. Morgan.

Dixon, Kenneth. British. 27, Alpha Street West, Salford 6, Lancs. Student. *Signed by:* J. R. Yates, P. G. Ashmore.

Dowden, Dennis Albert, B.Sc. (Bris.). British. 5, Crooksbarn Lane, Norton, Stockton-on-Tees. Technical Officer. *Signed by:* W. E. Garner, F. H. Pollard.

Drake, John Michael Francis. British. The Queen's College, Oxford. Undergraduate. *Signed by:* L. A. K. Staveley, J. W. Linnett.

Dyall, Leonard Kenneth. Australian. 137, Cleeland Street, Dandenong, Victoria, Australia. Student. *Signed by:* J. G. Scroggie, B. M. Lynch.

Emslie, Arthur Raymond Gordon, M.S.A. (Toronto), D.Sc. (Aberd.). Canadian. Chemistry Division, Science Service, Department of Agriculture, Ottawa, Canada. Chief of Chemistry Division. *Signed by:* O. E. Edwards, E. W. R. Steacie.

Fleifel, Abdallah Mohamed, M.Sc. and Ph.D. (Cairo). Egyptian. Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt. Lecturer. *Signed by:* M. I. Ali, M. A. Galaby.

Foster, Gordon, B.Sc. (Lond.). 17, Penywern Road, Earls Court, S.W.5. Research Student. *Signed by:* W. J. Hickinbottom, M. S. Grant.

Fraser, James, B.Sc. (Lond.), A.R.I.C. British. 45, Barden Road, Woodthorpe, Nottingham. Research Chemist. *Signed by:* G. R. Whalley, C. A. Bartram.

Friend, John, B.Sc. and Ph.D. (Liv.). British. Low Temperature Research Station, Downing Street, Cambridge. Civil Service Junior Research Fellow. *Signed by:* P. A. T. Swoboda, B. Coleby.

Garside, John Herbert. British. 114, Sturdee Avenue, Gillingham, Kent. Student. *Signed by:* R. F. Garwood, M. J. S. Dewar.

Gill, Edward William, B.A. (Oxon.). British. 30, Kilner House, Clayton Street, Kennington, S.E.11. Research Student at Corpus Christi College, Oxford. *Signed by:* D. Ll. Hammick, A. S. Bailey.

Gilreath, Esmarch Senn, M.A. and Ph.D. (North Carolina). American. Department of Chemistry, Washington and Lee University, Lexington, Virginia, U.S.A. Professor and Head of Chemistry Department. *Signed by:* A. Roe, J. F. Bunnett.

Goodburn, Terence George, B.Sc. (Sheffield). British. 164, Heath Road, Hounslow, Middlesex. Development Chemist. *Signed by:* D. S. Morris, L. G. Smith.

Gregor, Ian Kelvin, B.Sc. (New England). Australian. c/o N.S.W. University of Technology, Broadway, Sydney, Australia. Assistant Chemist with the Metropolitan Water Board. *Signed by:* R. L. Martin, C. M. Harris.

Hardie, Norman Francis. British. 15, Leopold Street, Leeds, 7. Clerical. *Signed by:* E. Rothstein, W. A. Wightman.

Harvey, Stephen Henry, B.Sc. and Ph.D. (Lond.). British. 122, Knighton Road, Leicester. Lecturer at University College, Leicester. *Signed by:* R. W. Bott, N. Macleod.

Haslam, Edwin, B.Sc. and Ph.D. (Sheffield). British. 22, Great North Road, Welwyn Garden City, Herts. Research Student. *Signed by:* J. Haslam, R. F. Webb.

Herbert, John Richards, B.Sc. (Bris.). British. 6, Osborne Road, Clifton, Bristol, 8. Research Student at Bristol University. *Signed by:* W. D. Ollis, W. Baker.

Hetherington, Gordon, B.Sc. (Dunelm), A.R.I.C. British. 7, Eastfield Avenue, Monkseaton, Whitley Bay, Northumberland. Research Chemist. *Signed by:* P. L. Robinson, G. A. Swan.

Holliday, Ivan Andrew, B.A. (Oxon.). British. Wadham College, Oxford. Student. *Signed by:* L. A. K. Staveley, N. Polgar.

Howarth, Joseph Simeon, B.Sc. (Birm.), A.R.I.C. British. 110, Newhall Street, Cannock, Staffs. Scientist with the National Coal Board, Cannock. *Signed by:* E. J. Bourne, J. C. Tatlow.

Jackson, Andrew Walter. British. 13, Blacket Avenue, Edinburgh, 7. Student. *Signed by:* G. O. Aspinall, D. Taylor.

Jain, Amolak Chand, M.Sc. and Ph.D. (Delhi). Indian. University Chemical Laboratory, Pembroke Street, Cambridge. Research student. *Signed by:* G. W. Kenner, S. Varadarajan.

Jain, Megh Kumar, M.Sc. (Panjab). Indian. c/o Department of Organic Chemistry, The University, Glasgow, W.2. Student. *Signed by:* T. Cohen, K. H. Overton.

Johnson, Leslie Cyril, B.A. (Cantab.). British. 20, Bergholt Crescent, London, N.16. Research Student at Cambridge University. *Signed by:* J. Harley-Mason, F. B. Kipping.

Johnston, Eric, B.A. (Oxon.). British. 64, Herschel Street, Everton, Liverpool, 5. Research Student. *Signed by:* L. A. K. Staveley, D. Ll. Hammick.

Johnston, Vera, B.A. (Oxon.). British. 27, Swaledale Gardens, High Heaton, Newcastle upon Tyne, 7. Research Chemist with B.C.U.R.A., Leatherhead, Surrey. *Signed by:* D. Hodgkin, P. H. Given.

Jones, William Arthur, B.Sc. (Lond.), A.R.I.C. British. 26, Brainton Avenue, Feltham, Middlesex. Research Chemist with Messrs. Parke-Davis & Co., Hounslow. *Signed by:* A. Campbell, E. N. Morgan.

Kirkaldy, David. British. 17, Industrial Street, Pelton, Chester-le-Street, Co. Durham. Student. *Signed by:* R. E. Ford, W. E. Addison.

Lauder, Ian, M.Sc. (New Zealand), Ph.D. (Manc.), D.Sc. (Queensland). Chemistry Department, University of Queensland, Brisbane, Australia. Associate Professor of Chemistry. *Signed by:* T. G. H. Jones, I. R. Wilson.

Lawrance, Derek Robert, A.R.I.C. British. 25, Poplar Road, Croesyceiliog, Cwmbran, Monmouthshire. Research Chemist. *Signed by:* K. Butler, W. A. W. Cummings.

Lee, John David, B.Sc. (Nott.). British. 58, Ribby Road, Kirkham, Preston, Lancs. Student. *Signed by:* F. C. Laxton, A. R. Mathieson.

Logan, Norman. British. 11, Queens Road, Shipley, Yorks. Student at Nottingham University. *Signed by:* C. C. Addison, J. C. Roberts.

Lord, George Harry, B.Sc. (Lond.). British. 25, de Bohun Avenue, Southgate, London, N.14. Research Student. *Signed by:* I. L. Finar, A. B. Simmonds.

Lukes, Robert Michael, Ph.D. (Notre Dame). American. 1928, Dean Street, Schenectady 9, New York, U.S.A. Research Associate at the General Electric Co. *Signed by:* I. S. Bengelsdorf, G. A. Russell.

McCaldin, Denis James, B.Sc. (Nott.). British. 16, Barrack Lane, The Park, Nottingham. Research Student. *Signed by:* A. W. Johnson, W. E. Addison.

Manning, Phillip Pleydell, M.A. and Ph.D. (Cantab.). British. 150, Marshalswick Lane, St. Albans, Herts. Research Chemist. *Signed by:* B. Mills, J. A. Fendley.

March, Peter James, B.Sc. (Lond.), A.R.I.C. British. c/o Egham Technical Service Laboratories, Whitehall Lane, Egham, Surrey. Laboratory Manager. *Signed by:* W. B. Hawes, F. J. Parmenter.

Markham, Edward. British. 83, Lady Bay Road, West Bridgford, Nottingham. Student. *Signed by:* C. C. Addison, T. J. King.

Marnef, Louis. Belgian. Fakkelstraat 45, Hoboken, Belgium. Technical Manager at Manufacture Belge de Rubans & Carbones, S.A., Antwerp. *Signed by:* A. Brewer, R. L. Barker.

Miles, David Hugh. British. Connaught Hall, Torrington Square, London, W.C.1. Student. *Signed by:* A. Maccoll, E. D. Hughes.

Mill, Theodore, B.S. (Wayne), American. Chemistry Department, University of Washington, Seattle 5, Washington, U.S.A. Graduate Student. *Signed by:* W. M. Schubert, K. B. Wiberg.

Miller, Glyn, B.A. (Oxon.). British. c/o Haventree, Kidderminster Road South, West Hagley, Stourbridge, Worcestershire. Research Chemist with Messrs. Albright & Wilson, Ltd. *Signed by:* G. D. Parkes, P. H. Carter.

Morris, Graeme Crocker, B.Sc. (Sydney). British. Christian Brothers' Training College, Strathfield, N.S.W., Australia. Teaching Fellow of the Chemistry School of the University of Sydney. *Signed by:* I. G. Ross, L. E. Lyons.

Moult, Peter Eric Geoffrey, B.A. (Oxon.). British. 13, St. Thomas' Drive, Hatch End, Middlesex. National Serviceman. *Signed by:* H. W. Thompson, E. J. Bowen.

Muir, William McClement. British. Mileburn House, 53, Ashton Road, Gourock, Renfrewshire. Student. *Signed by:* D. S. Payne, G. L. Buchanan.

Nelson, Robert Livingston. British. 54, Middleton Road, Uphall, Broxburn, West Lothian. Student at Edinburgh University. *Signed by:* J. H. Knox, G. O. Aspinall.

Nickels, Eileen Dorothy. British. Lynwood, 1208, London Road, Norbury, London, S.W.16. Assistant Chemist and Secretary. *Signed by:* H. E. Nickels, S. A. Ashmore.

O hEocha, Colm, M.Sc. (N.U.I.), Ph.D. (California). Irish. University College Galway, Ireland. Lecturer. *Signed by:* P. O Colla, E. Lee.

Parish, Richard Vernon, B.Sc. (Lond.). British. 59, The Avenue, Wembley Park, Middlesex. Student at University College, London. *Signed by:* P. W. C. Barnard, R. S. Nyholm.

Paton, Cumming, B.Sc. (Aberd.). British. 18, Carden Place, Aberdeen. Research Student. *Signed by:* R. H. Thomson, R. L. Hardie.

Paul, Albert Peter, B. S. (Penna.), M.A. (Swarthmore Coll.), Ph.D. (Columbia). American. 938, Park Avenue, Plainfield, New Jersey, U.S.A. Research Chemist. *Signed by:* W. L. Mosby, D. W. Hein.

Pickerell, Geoffrey Howard. British. Moorhurst, Grindleford, Nr. Sheffield. Undergraduate at Sheffield University. *Signed by:* J. Lewis, R. G. Wilkins.

Pinot de Moira, Peter Jules, B.Sc. (Lond.), A.R.I.C. British. 67, Monkhams Lane, Woodford Green, Essex. Research Chemist. *Signed by:* R. P. Royer, A. Tyrrell.

Price, Anthony Lloyd, B.A. (Oxon.). British. 30, Stile Road, Headington, Oxford. Student. *Signed by:* L. A. K. Staveley, D. Ll. Hammick.

Price, Charles C., Ph.D. (Harvard). American. Department of Chemistry, University of Pennsylvania, 34th and Spruce Streets, Philadelphia 4, Pa., U.S.A. Blanchard Professor of Chemistry. *Signed by:* P. George, J. O'M. Bockris.

Raphael, John George. British. 55, London Road, Ipswich, Suffolk. Laboratory Assistant with I.C.I., Ltd. (Paints Division). *Signed by:* W. H. Ferguson, R. Simpson.

Raynor, John Barrie. British. 21, Hillington Gardens, Woodford Green, Essex. Student. *Signed by:* C. C. Addison, H. Booth.

Reid, Allen Forrest, M.Sc. (New Zealand). British. 35, Tasmania Circle, Canberra, A.C.T., Australia. Research Scholar. *Signed by:* C. J. Wilkins, J. R. Richards.

Reusch, William Henry, B.S. (Michigan). American. Chemistry Department, Columbia University, New York 27, New York, U.S.A. Graduate Student. *Signed by:* R. R. Wittekind, R. A. L. Wilson.

Rosen, Arnold, B.Sc. (Lond.). British. 31, Portland Rise, London, N.4. Student. *Signed by:* R. F. Hudson, I. Stelzer.

Rowlingson, Donald Malcolm. British. Westgate Street, Southery, Downham Market, Norfolk. Student. *Signed by:* A. R. Mathieson, C. C. Addison.

Salama, Adib, B.Sc. (Cairo), M.Sc. (Alexandria), Ph.D. (Lond.). Egyptian. Chemistry Department, University of Glasgow, Glasgow, W.2. Assistant in Chemistry. *Signed by:* E. Gelles, D. S. Payne.

Salem, Tahani Mahmoud, (Mrs.), M.Sc. and Ph.D. (Cairo). Egyptian. Womens Institute, Zamalek, Em Shams University, Cairo, Egypt. Lecturer. *Signed by:* A. M. El-Abbady, L. S. H. El-Assal.

Salter, Roy, B.A. (Oxon.). British. 29, Coleridge Road, Crouch End, London, N.8. Student. *Signed by:* E. J. Bowen, M. V. Kelemen.

Sanders, Hans Thomas. British. 4, Vaughan Avenue, Hendon, London, N.W.4. Undergraduate Student at University College, London. *Signed by:* A. Maccoll, D. J. Millen.

Scott, John Marshall William, B.Sc. (Lond.). British. 32, Tanys Dell, Harlow, Essex. Scientific Officer, Admiralty, Harlow. *Signed by:* M. J. S. Dewar, W. J. Hickinbottom.

Scott, William Peter. British. 2, Empire Road, Carlisle, Cumberland. Student at Nottingham University. *Signed by:* C. C. Addison, H. Booth.

Shooter, Douglas. British. 31, Albert Avenue, Jacksdale,Notts. Student at Nottingham University *Signed by:* C. C. Addison, T. J. King.

Skidmore, Sydney, B.Sc. (Lond.), A.R.I.C. British. 29, Central Drive, Ansdell, Lytham-St.-Annes, Lancs. Lecturer at the Royal Technical College, Salford. *Signed by:* G. R. Ramage, H. Suschitzky.

Slater, Keith. British. 211, Abbeyhills Road, Oldham, Lancs. Student at Leeds University. *Signed by:* E. Rothstein, J. A. S. Smith.

Smith, Barry Charles, B.A. (Cantab.). British. 30 Melstock Avenue, Upminster, Essex. Demonstrator in Inorganic Chemistry. *Signed by:* F. C. Laxton, C. C. Addison.

Stace, Brian Carl, B.Sc. (Lond.). British. 205, Harlesden Road, London, N.W.10. Postgraduate Student. *Signed by:* H. G. Poole, A. Maccoll.

Stephen, Edith, M.Sc. (Witwatersrand). South African. Imperial College Hostel, Prince Consort Road, London, S.W.7. Student. *Signed by:* M. Whalley, J. A. Elvidge.

Stonner, Frederik Willem, M.Sc. and Ph.D. (New Brunswick). Canadian. Apartment 1-I, 419 West 119 Street, New York 27, New York, U.S.A. Research Assistant at Columbia University. *Signed by:* R. R. Wittekind, R. A. L. Wilson.

Taylor, John Boris, M.Sc. and Ph.D. (Manc.), A.R.I.C. British. 140, Musters Road, West Bridgford, Nottingham. Research Chemist with British Plaster Board (Holdings) Ltd., East Leake, Nr. Loughborough. *Signed by:* J. S. Rowlinson, E. Warhurst.

ten Haken, Pieter. Dutch. 7, Bournemouth Drive, Herne Bay, Kent. Research Chemist. *Signed by:* F. H. Newth, J. Yates.

Thomas, Colin Reginald, M.Sc. (Wales), A.R.I.C. British. 267, Worthing Road, Basingstroke, Hants. Research Chemist at Atomic Weapons Research Establishment, Aldermaston. *Signed by:* J. C. Tatlow, M. Stacey.

Thomas, Daniel James, B.Sc. (Lond.). British. 94, London Road, High Wycombe, Bucks. Postgraduate Student. *Signed by:* E. D. Hughes, C. A. Bunton.

Vallarino, Lydia, Dr.Ind.Chem. (Milan). Italian. Via Mangiagalli 18, Milano, Italy. Assistant Professor of General Chemistry at Milan University. *Signed by:* L. Malatesta, M. Simonetta.

Ward, Richard Bernard, B.Sc. (Birm.), A.R.I.C. British. Chemistry Department, The University, Birmingham, 15. Student. *Signed by:* M. Stacey, E. J. Bourne.

Warford, Ernest William Thomas, M.Sc. (Lond.). British. 7, Preen Drive, Middlesbrough, Yorks. Technical Officer with I.C.I. Ltd., Billingham Division. *Signed by:* D. C. Eagles, R. Pettit.

Waters, David Neil, B.A. (Oxon.). British. 31, The Fairway, New Barnet, Herts. Student at Oxford University. *Signed by:* L. A. K. Staveley, L. A. Woodward.

Webber, John Michael, B.Sc. (Birm.). British, Crantock, Little Johns Cross Hill, Exeter. Research Student at Birmingham University. *Signed by:* J. C. Tatlow, A. B. Foster.

Weiss, Karl H., B.S. (Columbia). American. 1521, Undercliff Avenue, New York 53, N.Y., U.S.A. Instructor in Chemistry at New York University. *Signed by:* K. Mislow, H. M. Hellman, S. C. Dickerman.

Wellings, Ian. British. 39, Bradfield Avenue, Kelvindale, Glasgow, W.2. Student at Glasgow University. *Signed by:* S. H. Tucker, J. C. Speakman.

Withey, Raymond James. British. 4, Clavering Road, Wanstead, London, E.12. Undergraduate at Queen Mary College, London. *Signed by:* M. F. Ansell, R. F. Garwood.

Woodhams, Patricia Maureen. British. Imperial College Hostel, Prince Consort Road, London, S.W.7. Student at Imperial College. *Signed by:* J. A. Elvidge, M. Whalley.

Wraigs, John Douglas Michael. British. 9, Glenesk Road, Eltham Park, London, S.E.9. Student. *Signed by:* S. R. Landor, P. D. Landor.

Wright, Alexander Neill, B.A. (Oxon.). British. Southfield House, Belhaven Road, Dunbar, East Lothian. Research Student. *Signed by:* M. C. Ford, R. H. Thomson.

Zeller, Alfred, Dr.Phil. (Vienna). Austrian. 84, Hills Avenue, Cambridge. Research at Chesterford Park Research Station, Saffron Walden. *Signed by:* G. S. Hartley, A. J. Lambie.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Adamcik, Joe Alfred, B.S. and M.A. (Texas). American. 219, Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A. Graduate Student. *Signed by:* D. Y. Curtin.

Allinger, Janet, B.S. and Ph.D. (California). American. Converse Memorial Laboratories, Harvard University, Cambridge 38, Massachusetts, U.S.A. Research Assistant. *Signed by:* H. Hart.

Bacchus, Abdul Latif. c/o Miss L. Segre, Chatsworth, Savanna-la-Mar, Jamaica, B.W.I. Cane Farmers' Chemist. *Signed by:* H. Paul.

Dutta, Phanindra Chandra, D.Sc. (Calcutta). Indian. Indian Association for the Cultivation of Science, Jadavpur, Calcutta, 32, India. Professor and Head of the Department of Organic Chemistry. *Signed by:* S. R. Palit.

Elmezzi, Thomas. American. c/o Pepsi-Cola Company, 46—02 Fifth Street, Long Island City 1, New York, U.S.A. Vice-President. *Signed by:* A. H. Moore.

Finestone, Arnold B., B.A. (New York), Ph.D. (Polytechnic Inst. of Brooklyn). American. Westinghouse Research Laboratory, Churchill Boro, Pittsburgh 35, Penna., U.S.A. Research Chemist. *Signed by:* A. Dobry.

Finzi, Cesare. Italian. Istituto di Chimica Farmaceutica, Universita di Perugia, Italy. Professor of Pharmaceutical Chemistry. *Signed by:* V. Bellavita.

Fischer, Carl Wilhelm. American. 35—31 203rd Street, Bayside 61, N.Y., U.S.A. Assistant to Vice-President in charge of Manufacturing, Pepsi-Cola Co. *Signed by:* A. H. Moore.

Hediger, Hans Jorg, Dr.sc.tech. (E.T.H., Zurich). Swiss. Kilchbergstr. 129, Zurich 2/38, Switzerland. Application Engineer, c/o Perkin-Elmer, A.G., Zurich. *Signed by:* G. W. Kenner.

Katz, Herbert C., B.S. (Roosevelt Coll.). American. 3750 N. Pine Grove Avenue, Chicago 13, Illinois, U.S.A. Research Chemist. *Signed by:* L. B. Wick.

Kincl, Fred Allan, Dipl.Ing.Chem. (Tech. Hochschule, Prague). American. c/o Syntex S.A., Apdo. Postal 2679, Mexico, D.F. Research Chemist. *Signed by:* O. Mancera.

Long, Louis, jun., B.S. (Princeton), S.M. (M.I.T.), M.A. and Ph.D. (Harvard). American. Carr Road, Concord, Massachusetts, U.S.A. Organic Research Chemist. *Signed by:* G. M. Wyman.

McGuire, Francis Joseph, B.S. (Loyola Coll.). American. Dale Road, R.R. No. 4, Box 35, Riviera Beach, Pasadena, Maryland, U.S.A. Graduate Student at Johns Hopkins University. *Signed by:* A. Nickon.

Marvell, Elliot Nelson, B.S. (Brown), Ph.D. (Ill.). American. Department of Chemistry, Oregon State College, Corvallis, Oregon, U.S.A. Assistant Professor of Organic Chemistry. *Signed by:* T. E. King.

Milian, Alwin S., jun., B.S. (M.I.T.). American. Department of Chemistry, University of California, Berkeley 4, California, U.S.A. Student. *Signed by:* A. Streitwieser.

Miller, Robert Clay, B.S. (Northeastern), A.M. (Columbia), Ph.D. (Temple). American. 240, Lexington Avenue, Pitman, New Jersey, U.S.A. Research Chemist with the Socony Mobil Oil Co. Inc., New Jersey. *Signed by:* L. A. Hamilton.

Murr, Brown Lewis, jun., B.A. and M.S. (Emory). American. 9111th TU., Quartermaster Research and Development Command, Natick, Massachusetts, U.S.A. Chemist. *Signed by:* G. M. Wyman.

Natarajan, C., B.Sc. (Madras), M.A. and M.Sc. (Annamalai). Indian. No. 2 Dalay Road, Vepery, Madras-7, South India. *Signed by:* V. Baliah.

Rahman, Mohammed Hafizur, B.Sc. (Dacca). Pakistani. 25, Nuton Bazar Crossing, P.O. Mymensingh, East Pakistan. Sales Representative of Imperial Chemical Industries (Pakistan), Ltd., Dacca. *Signed by:* K. S. Mohamad.

Ratney, Ronald Steven, B.S. (Calif. Inst. of Tech.), M.S. (Yale). American. Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut, U.S.A. Student. *Signed by:* H. H. Wasserman.

Steinberg, George M., M.S. and Ph.D. (Purdue). American. P.O. Box 858, Edgewood, Maryland, U.S.A. Chemist. *Signed by:* R. E. Plapinger.

Stevens, John David, B.Sc. (Tasmania). British. The University of New England, Armidale, 5N, N.S.W., Australia. Research Assistant. *Signed by:* N. V. Riggs.

von Bezard, André, Dr.Phil. (Vienna). Austrian. 24, Rue Vermont, Geneva, Switzerland. European Research Associate of Du Pont de Nemours & Co., Wilmington. *Signed by:* H. Lewis.

PAPERS ACCEPTED

(List of Papers accepted between February 20th and March 21st, 1956, for publication in the *Journal*.)

"Some reactions of hæmatoxylin." By D. J. Duff.

"The effect of sulphur dioxide on the oxidation of copper." By T. Mills and U. R. Evans.

"The lowest singlet excited levels of naphthalene. Part II. Some relations between various approximations." By R. Lefebvre and C. M. Moser.

"The oxidation of chromous perchlorate solutions by molecular oxygen." By Michael Ardon and Gabriel Stein.

"The effect of peptising agents on the crystal growth of insoluble metal salts. Part I. Precipitation in aqueous solution." By A. Packter.

"Alkylperoxy-radicals. Part II. Kinetics of autoxidations retarded by 2 : 4 : 6-trialkylphenols." By A. F. Bickel and E. C. Kooyman.

"A new chromatographic procedure and its application to high polymers." By C. A. Baker and R. J. P. Williams.

"An *X*-ray examination of the crystal structure of *p*-iodonitrosobenzene." By Monica S. Webster.

"Constitution of tamarind-seed polysaccharides and the structure of the xylan." By G. R. Savur.

"The alkaline hydrolysis of phosphonate esters." By R. F. Hudson and L. Keay.

"The hydrolysis of di*iso*propyl methylphosphonodithiolate." By R. F. Hudson and L. Keay.

"The morphine–thebaine group of alkaloids. Part VI. The condensation of thebaine with dienophiles." By K. W. Bentley and A. F. Thomas.

"The morphine–thebaine group of alkaloids. Part VII. A new method of systematic degradation to nitrogen-free products." By K. W. Bentley, J. C. Ball, and J. P. Ringe.

"The intensity of ultraviolet light absorption by monocrystals. Part I. Measurement of thickness of thin crystals by interferometry." By A. Bree and L. E. Lyons.

"The intensity of ultraviolet light absorption by monocrystals. Part II. Absorption and reflection by anthracene of plane polarised light." By A. Bree and L. E. Lyons.

"Kinetics of the reaction between benzoyl peroxide and phenols." By J. J. Batten and M. F. R. Mulcahy.

"Structural effects in the reaction between benzoyl peroxide and phenols." By J. J. Batten.

"Steroids and Walden inversion. Part XXXI. The 3 : 5-*cyclo*steroid rearrangement." By C. W. Shoppee and D. F. Williams.

"The heats of combustion of quinol and *p*-benzoquinone, and the thermodynamic quantities of the oxidation–reduction reaction." By G. Pilcher and L. E. Sutton.

"Organic retentions in neutron-irradiated bromobenzene." By M. Milman and P. F. D. Shaw.

"Carcinogenic nitrogen compounds. Part XIX. The aptitude of some aminoquinolines for cyclisation." By Ng. Ph. Buu-Hoï, Rene Royer, and Michel Hubert-Habart.

"Tetrazolium compounds. Part V. Polarography of triphenyltetrazolium bromide and some of its substituted derivatives." By H. Campbell and P. O. Kane.

"Stereochemistry of *cyclo*hexane derivatives. Part III. The hydroxylation of (+)-*trans*-*p*-menth-2-ene." By P. R. Jefferies and B. Milligan.

"The relative tendencies of simple monoamines to form co-ordination compounds. The stability constants of some amine–platinous complexes." By J. Chatt and G. A. Gamlen.

"The effect of solvent on a simple ion–dipole reaction. Part I. The order and mechanism of the methyl iodide–iodide ion-exchange reaction in different solvents." By E. R. Swart and L. J. le Roux.

"The kinetics and mechanisms of some colour reactions of aromatic nitro-compounds at low temperatures. Part II. 2 : 4 : 6-Trinitroanisole." By J. B. AINSCOUGH and E. F. CALDIN.

"The kinetics and mechanisms of some colour reactions of aromatic nitro-compounds at low temperatures. Part III. s-Trinitrobenzene." By J. B. AINSCOUGH and E. F. CALDIN.

"The kinetics and mechanisms of some colour reactions of aromatic nitro-compounds at low temperatures. Part IV. 2 : 4 : 6-Trinitrotoluene : a second reaction with ethoxide ion." By J. B. AINSCOUGH and E. F. CALDIN.

"The interaction of aluminium bromide with olefins and with benzene." By FRED FAIRBROTHER and KENNETH FIELD.

"The chemistry of ψ-santonin. Part X." By N. M. CHOPRA, WESLEY COCKER, J. T. EDWARD, T. B. H. MCMURRY, and E. R. STUART.

"Absorption spectra and structure of some solid hydroxyazo-compounds." By D. HADŽI.

"The reaction of triphenyl phosphite with the halogens." By G. S. HARRIS and D. S. PAYNE.

"The organic chemistry of phosphorus. Part III. The nature of the products formed by the action of halogens on triphenyl phosphite." By H. N. RYDON and B. L. TONGE.

"The activation of carbon–carbon double bonds by cationic catalysts." Part II. The effect of *para*-substituents and of solvent on the dimerisation of diarylethylenes." By ALYWN G. EVANS, N. JONES, PETER M. S. JONES, and J. H. THOMAS.

"Trichloromethylthio-derivatives of biological interest." By GEORGE SOSNOVSKY.

"Electrochemical studies on polonium." By K. W. BAGNALL and J. H. FREEMAN.

"Congeners of pyridine-4-carboxyhydrazide. Part I. Derivatives of 4-cyanopyridine and 2-cyanothiazole." By D. D. LIBMAN and R. SLACK.

"The stability of coumarinic acids. Chelation of the hydroxyl group." By MALCOLM CRAWFORD and J. W. RASBURN.

"Molecular polarisability. The molar Kerr constants of benzyl alcohol and aniline at infinite dilution." By M. ARONEY and R. J. W. LE FÈVRE.

"The ionization of ethyleneimine and polyethyleneimine." By E. J. SHEPHERD and J. A. KITCHENER.

"Oxygen heterocycles. Part V. A study in phenoxathiin derivatives." By ELIE LESCOT, NG. PH. BUU-HOÏ, and N. D. XUONG.

"Quinoxaline *N*-oxides. Part IV. Derivatives of *Py*-hydroxyalkyl-, -aminoalkyl-, and -carboxy-quinoxalines." By J. K. LANDQUIST and J. A. SILK.

"Quinoxaline *N*-oxides. Part V. Further *Bz*-substituted derivatives." By J. A. SILK.

"Some reactions of 2-chlorophenazine 5 : 10-dioxide." By JUSTUS K. LANDQUIST.

"Quinoxaline *N*-oxides. Part VI. *N*-Oxides of 2 : 3-polymethylenequinoxalines." By JUSTUS K. LANDQUIST.

"The determination of acid strengths of organic hydroperoxides." By D. BARNARD, K. R. HARGRAVE, and G. M. C. HIGGINS.

"Aliphatic hydroxylamines. Part III. Reaction with diazotised aromatic amines. A novel synthesis of acylbenzenes from the corresponding amine." By M. A. THOROLD ROGERS.

"Potential antiviral thiourea derivatives." By NG. PH. BUU-HOÏ, NG. D. XUONG, and NG. H. NAM.

"The nucleotide sequence in deoxypentosenucleic acids. Part I. The action of mercaptoacetic acid on calf-thymus deoxyribonucleic acid." By A. S. JONES and D. S. LETHAM.

"The nucleotide sequence in deoxypentosenucleic acids. Part II. The alkaline degradation of calf-thymus *aldehydo*apurinic di(carboxymethyl) dithioacetal." By A. S. JONES, D. S. LETHAM, and M. STACEY.

" The nucleotide sequence in deoxypentosenucleic acids. Part III. The nature of the end groups produced by the alkaline hydrolysis of calf-thymus *aldehydo*apurinic acid di(carboxymethyl) dithioacetal." By A. S. JONES, D. S. LETHAM, and M. STACEY.

" Synthesis of divicine (2 : 4-diamino-5 : 6-dihydroxypyrimidine) and other derivatives of 4 : 5(5 : 6)-dihydroxypyrimidine." By J. DAVOLL and D. H. LANEY.

" The preparation of some substituted pyridine 1-oxides." By A. R. KATRITZKY.

" Polymerisation of thiophen derivatives. Part V. The self condensation of 4 : 5- and 6 : 7-benzothionaphthen 1 : 1-dioxides. A new route to 1-1'- and 4-2'-naphthylphenanthrene." By W. DAVIES and Q. N. PORTER.

" Pteridine derivatives. Part II. Methylation of 2 : 4-dihydroxy-6- and 7-phenylpteridine, and related topics." By G. P. G. DICK, H. C. S. WOOD, and (in part) W. R. LOGAN.

" *cyclo*Hexane derivatives. Part II. The mechanism of catalytic hydrogenation of cyclic compounds." By R. J. WICKER.

" The enzymic synthesis and degradation of starch. Part XXII. Evidence of multiple branching in waxy-maize starch. A correction." By STANLEY PEAT, W. J. WHELAN, and GWEN J. THOMAS.

" An attempted synthesis of pelletierine." By R. E. BOWMAN and D. D. EVANS.

" Caulosapogenin and its identity with hederagenin." By J. MCSHEFFERTY and J. B. STENLAKE.

" 2-Methylbut-2-ene nitrosochloride and its derivatives." By N. THORNE.

" *epi*Pregnanolone–benzophenone adduct." By K. R. BHARUCHA.

" Griseofulvin. Part X. The orientation of some derivatives of 5-methoxyresorcinol." By JOHN FREDERICK GROVE, P. W. JEFFS, and D. W. RUSTIDGE.

" Studies in mycological chemistry. Part V. Synthesis of 2 : 5-dihydroxy-7-methyl-1 : 4-naphthaquinone." By J. E. DAVIES and JOHN C. ROBERTS.

" Pyrimidines. Part I. The synthesis of some 5-hydroxypyrimidines." By R. HULL.

" The rates of solvolysis of certain arylmethyl chlorides, and a simple molecular-orbital treatment of this and similar reactions." By M. J. S. DEWAR and R. J. SAMPSON.

" The preparation and properties of pyridino(1' : 2'-2 : 3)-1-oxa-2 : 4-diazol-5-one." By A. R. KATRITZKY.

" Gibberellic acid. Part III. Synthesis of fluorenone-4 : 5-dicarboxylic acid." By T. P. C. MULHOLLAND and G. WARD.

" Potential antituberculosis agents of the indole series." By F. P. DOYLE, (MRS.) W. FERRIER, D. O. HOLLAND, M. D. MEHTA, and J. H. C. NAYLER.

" Palladised charcoal as a catalyst for the reduction of aromatic nitro-compounds by hydrazine hydrate." By M. J. S. DEWAR and T. MOLE.

" The anodic oxidation of copper–tin (speculum) alloys at very low current density." By (the late) S. E. S. EL WAKKAD, T. M. SALEM, A. M. SHAMS EL DIN, and Z. HANAFI.

" Triterpenoids. Part LI. The isolation and characterisation of glabric acid, a new triterpenoid acid from liquorice root." By J. M. BEATON and F. S. SPRING.

" The extraction of indium bromide into mixed organic solvents." By H. IRVING and F. J. C. ROSSOTTI.

" 3 : 4-Dihydro-4-phenyl-carbostyril and -*iso*carbostyril and some of their derivatives." By (Miss) E. F. M. STEPHENSON.

" Studies in pyrolysis. Part VI. Competitive routes in the pyrolysis of acyl cyanides and their dimeric forms." By R. N. BENNETT, E. JONES, and P. D. RITCHIE.

" Determination of the degree of polymerisation of reducing oligosaccharides." By STANLEY PEAT, W. J. WHELAN, and J. G. ROBERTS.

" Pteridine studies. Part VIII. The degradation of pteridine. Methylation of the hydroxypteridines and degradation of the products." By ADRIEN ALBERT, D. J. BROWN, and H. C. S. WOOD.

" Constituents of the lipids of tubercle bacilli. Part VII. Synthesis of (+)-2(*L*) : 4(*L*)-dimethyldocosanoic acid, an oxidation product of mycolipenic acid." By G. I. FRAY and N. POLGAR.

" The formation of phenyl radicals from tetraphenyl-lead." By J. E. SPICE and W. TWIST.

" Demethoxykanugin : a new crystalline compound from *Pongamia glabra*." By O. P. MITTAL and T. R. SESHADRI.

" The reaction of 2-acetamido-2-deoxy-D-glucose with ethanethiol and hydrochloric acid." By L. HOUGH and MAHMOUD I. TAHA.

" The relation between configuration and conjugation in diphenyl derivatives. Part VI. Some alkyldiphenyls." By PAULINE M. EVERITT, D. MURIEL HALL, and E. E. TURNER.

" Some derivatives of kojic acid." By M. G. BROWN.

" Some reactions involving multiplicity changes." By DOUGLAS CLARK and H. O. PRITCHARD.

" Hydroxylations with potassium manganate." By W. RIGBY.

" 11-Sulphoundecanoic acid." By W. RIGBY.

" Studies on specific chemical fission of peptide links. Part II. The preparation and hydrolysis of 1-acylpyrrolid-2-ones derived from α-glutamylpeptides." By ALAN R. BATTERSBY and J. C. ROBINSON.

" A crystallographic study of trismethylsulphonylmethane." By S. C. ABRAHAMS and J. C. SPEAKMAN.

" Heat capacity and entropy of trismethylsulphonylmethane." By T. DAVIES and L. A. K. STAVELEY.

" Studies in the xanthone series. Part I." By (the late) S. H. DAVIES, F. SCHEINMANN, and H. SUSCHITZKY.

" The soluble polyglucose of sweet corn (Zea mays)." By STANLEY PEAT, W. J. WHELAN, and J. R. TURVEY.

" Hybridization in the ground state of the hydrogen molecule-ion." By B. F. GRAY, H. O. PRITCHARD, and F. H. SUMNER.

" The conductivity of solutions in which the solvent molecule is ' large.' II. Solutions of tetrapentylammonium picrate in some phthalate esters." By C. M. FRENCH and N. SINGER.

" Usnic acid. Part XII. Pummerer's ketone." By VINCENT ARKLEY, F. M. DEAN, ALEXANDER ROBERTSON, and PADET SIDISUNTHORN.

" The anodic behaviour of lead in halide solutions." By G. W. D. BRIGGS and W. F. K. WYNNE-JONES.

" 1 : 8-Dihydroxynaphthalene." By NG. PH. BUU-HOÏ and DENISE LAVIT.

" Triterpenoids. Part LII. The constitution and stereochemistry of friedelin and cerin." By GEORGE BROWNLIE, F. S. SPRING, ROBERT STEVENSON, and W. S. STRACHAN.

" Structural chemistry of the alkoxides. Part VI. Primary alkoxides of quadrivalent cerium and thorium." By D. C. BRADLEY, A. K. CHATTERJEE, and W. WARDLAW.

" The synthesis of 7-(2 : 3-dihydroxypropyl)theophylline." By DAVID B. ISHAY.

" Colombo-root bitter principles. Part II. The constitution of columbin." By D. H. R. BARTON and DOV ELAD.

" An approach to the total synthesis of triterpenes. Part I." By T. G. HALSALL and D. B. THOMAS.

" The preparation of 7-methyl-2-naphthol." By T. G. HALSALL and D. B. THOMAS.

" Terpenes. Part X. A synthesis of (±)-angustione." By J. C. BARDHAN and R. N. ADHYA.

" The constitution of the neutral, tetracyclic triterpenes of dammar resin." By J. S. MILLS.

" The structure of isatin and substituted isatins." By D. G. O'SULLIVAN and P. W. SADLER.

" Electrometric titration of the sodium salts of deoxyribonucleic acids. Part IV. Denaturation by heating in aqueous solution." By R. A. COX and A. R. PEACOCKE.

" Benzoyloxylation, halogenation, and phenylation of aromatic compounds by silver bromide dibenzoate and silver iodide dibenzoate." By D. BRYCE-SMITH and PETER CLARKE.

"Normal alkoxides of quinquevalent niobium." By D. C. BRADLEY, B. N. CHAKRAVARTI, and W. WARDLAW.

"Nucleotides. Part XXXVII. The structure of uridylic acids *a* and *b* and a synthesis of spongouridine (3-β-D-arabofuranosyluracil)." By D. M. BROWN, SIR ALEXANDER TODD, and S. VARADARAJAN.

"The structures of some acyl cytosines." By D. M. BROWN, SIR ALEXANDER TODD, and S. VARADARAJAN.

"Phthalaldehydes and related compounds. Part VII. Further applications of the *N*-bromosuccinimide preparative method." By JOHN BLAIR, W. R. LOGAN, and G. T. NEWBOLD.

"Absorption spectra of ketones. Part IV. The steric requirements for spectroscopic interaction between a carbonyl group and a βγ-double bond." By R. C. COOKSON and N. S. WARIYAR.

"Chlorophyll and related compounds. Part IV. The position of the extra hydrogen atoms in chlorophyll. The oxidation of pyrophæophorbide-*a*." By G. E. FICKEN, R. B. JOHNS, and R. P. LINSTEAD.

"Chlorophyll and related compounds. Part V. The dihydrohæmatinic acids and their imides." By G. E. FICKEN, R. B. JOHNS, and R. P. LINSTEAD.

"Further crystalline constituents of gum mastic." By ELISEO SEOANE.

"Stereochemical aspects of aromatic substitution. Part I. *peri*-Derivatives of naphthalene." By F. BELL, J. A. GIBSON, and R. D. WILSON.

"Stereochemical aspects of aromatic substitution. Part II. Derivatives of *tert.*-butylbenzene." By F. BELL and R. D. WILSON.

ADDITIONS TO THE LIBRARY

Organic syntheses in electrical discharges, by D. N. Andreyev. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Wavelength data and correction tables for length interferometry, by C. F. Bruce. (National Standards Laboratory Technical Paper No. 8.) Commonwealth Scientific and Industrial Research Organisation, Melbourne. 1956. (Presented by the Publishers.)

Chemical engineering cost estimation, by Robert S. Aries and Robert D. Newton. McGraw-Hill. 1955.

Chemistry of isotopes, by A. I. Brodskii. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Neurochemistry : the chemical dynamics of brain and nerve, edited by K. A. C. Elliott, Irvine H. Page, and J. H. Quastel. Charles C. Thomas. 1955.

Experiments in organic chemistry, by L. Fieser, 3rd edn. D. C. Heath & Co. 1955.

Production of nitric acid, by I. D. Fotinich. (In Russian.) 1950. (Presented by the U.S.S.R. Academy of Sciences.)

The collected papers of C. S. Hudson, edited by Raymond M. Hann and Nelson K. Richtmyer. 2 vols. Academic Press. 1946—48. (Presented by E. S. Lower.)

Standard methods for testing petroleum and its products, 15th edn. Institute of Petroleum. 1956.

International Symposium on Macromolecular Chemistry. Milano-Torino, 26 settembre–2 ottobre 1954. (Supplemento a " La Ricerca Scientifica," Anno 25°—1955.) Consiglio Nazionale delle Ricerche, Comitato Nazionale per la Chimica. 1955.

Chemical thermodynamics, by M. Kh. Karapet'yants. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Methods used in high molecular organic chemistry, by V. V. Korshak. Vol. I. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

The economic prospects of chemical industries in India, by A. K. Madan. Thacker and Co. 1949. (Presented by R. C. Madan.)

Chemistry of motor fuels, by A. D. Petrov. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Catalytic aromatisation of paraffin hydrocarbons, by A. F. Plate. (In Russian.) 1948. (Presented by the U.S.S.R. Academy of Sciences.)

Steroid chains as components of protein and carbon molecules, by T. van Schelven. Kosmos Publ. Co. 1946. (Presented by E. S. Lower.)

Hydrogen peroxide, by Walter C. Schumb, Charles N. Satterfield, and Ralph L. Wentworth. (American Chemical Society Monograph Series, No. 128.) Reinhold Publ. Corp. 1955.

Spot tests, by N. A. Tananaev. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

Materials handbook. Part IV. Properties of titanium, by Harry Majors, jun., R. T. Webster, R. H. Wallace, and G. E. Wendell. Part VII. Properties of tantalum, by Harry Majors, jun., R. H. Wallace, R. T. Webster, and G. E. Wendell. Part VIII. Properties of molybdenum, by Harry Majors, jun., R. H. Wallace, G. E. Wendell, and R. T. Webster. (United States Atomic Energy Commission.) U.S. Government Ptg. Office. 1953.

12th report of the committee on catalysis. (United States) National Research Council. Wiley. 1940. (Presented by E. S. Lower.)

A text-book of practical organic chemistry, including qualitative organic analysis, by A. I. Vogel, 3rd edn. Longmans. 1956. (Presented by the Author.)

Praktikum der organisch-präparativen pharmazeutischen Chemie und Leitfaden der chemischen Arzneimittelanalyse, by K. Winterfeld. 4. Aufl. Steinkopff. 1955.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	H. B. Henbest, Ph.D., A.R.C.S., A.R.I.C., Chemistry Department, The University, Manchester, 13.
,,	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
,,	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham.	C. C. Addison, D.Sc., Ph.D., F.R.I.C., Chemistry Department, The University, University Park, Nottingham.
Oxford.	L. A. K. Staveley, M.A., Inorganic Chemistry Laboratory, South Parks Road, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.
,,	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows :

	Elected.	Died.
Edmund Arthur Buckle (Hove)	Dec. 5th, 1912.	Nov. 9th, 1955.
Arthur Fred Campbell (Torquay)	June 20th, 1912.	Feb. 27th, 1956.
Albert Edward Garrett (Newton Abbot)	Feb. 20th, 1913.	Nov. 17th, 1955.
Edgar Archibald Morris (Glasgow)	Aug. 21st, 1947.	Feb. 12th, 1956.
Harold Picton (Watford)	Apr. 17th, 1890.	Mar. 21st, 1956.
James Porter Shenton (Sunbury-on-Thames) ...	June 17th, 1897.	Feb. 24th, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows who completed sixty years of Fellowship on May 5th, 1956 :

John McCrae (Johannesburg).
Henry Fishwick Robinson (Ashford, Derbyshire).

and to the following who completed fifty years of Fellowship on May 3rd, 1956 :

James Stuart Hills (S.E. 26).
William Tabor Lattey (Hove).
Foster Sproxton (East Barnet).
George Augustus Turner (Worcester).

ACKNOWLEDGMENTS.

The thanks of the Council have been conveyed to Dr. R. Lessing for a gift of the Society's publications and to a Life Fellow of the Society, who wishes to remain anonymous, for a donation to the Society's funds.

COMMITTEES 1956—1957.

The thanks of the Council have been conveyed to the retiring Members of Committees for the services they have rendered to the Society. The following have been appointed for 1956—1957 :

Finance and General Purposes Committee

Professor H. Burton, Dr. F. Hartley, Sir Cyril Hinshelwood, Dr. R. Holroyd, Professor E. D. Hughes, Professor E. R. H. Jones, Professor H. W. Melville, Sir Owen Wansbrough-Jones, together with the Officers, the Chairman of the Publication Committee, and the Representative of the Joint Library Committee on the Council of the Chemical Society, with the President as Chairman, Treasurer as Vice-Chairman, and the General Secretary as Secretary.

Research Fund Committee

Professor Wilson Baker, Professor C. E. H. Bawn, Professor H. J. Emeléus, Professor G. Gee, Professor D. H. Hey, Professor E. D. Hughes, Dr. F. E. King, Professor J. M. Robertson, Mr. R. M. Winter, together with the Officers, with the President as Chairman, and the General Secretary as Secretary.

Publication Committee

Professor C. K. Ingold (Chairman), Dr. C. C. Addison, Dr. G. Baddeley, Professor D. H. R. Barton, Professor E. Boyland, Dr. P. B. D. de la Mare, Professor H. J. Emeléus, Professor D. H. Everett, Professor G. Gee, Dr. B. A. Hems, Dr. H. R. Ing, Dr. H. M. N. H. Irving, Dr. D. J. G. Ives, Professor E. R. H. Jones, Dr. G. W. Kenner, Professor H. C. Longuet-Higgins, Professor B. Lythgoe, Professor R. A. Morton, Professor A. Neuberger, Professor R. G. W. Norrish, Dr. V. Petrow, Mr. H. M. Powell, Dr. P. L. Robinson, Dr. K. Schofield, Dr. N. Sheppard, Professor M. Stacey, Professor H. W. Thompson, Professor E. E. Turner, Professor A. R. J. P. Ubbelohde, and the Officers, with the Editor as Secretary.

Awards Committee

The President (Chairman), the immediate Past-President (Professor W. Wardlaw), Professor R. D. Haworth, Sir Cyril Hinshelwood, Professor C. K. Ingold, Professor H. W. Melville, Dr. R. Spence, Sir Alexander Todd, with the General Secretary as Secretary.

HONORARY FELLOWS.

The following have been nominated by the Council for election as Honorary Fellows of the Chemical Society in accordance with the terms set out in Part II of the Bye-Laws of the Society:

Professor R. S. Mulliken (Chicago), distinguished for his researches in spectroscopy and in the application of wave-mechanics to chemistry.

Professor R. B. Woodward (Harvard), distinguished for his contributions to synthetic organic chemistry.

THE HARRISON MEMORIAL PRIZE

In accordance with the Trust Deed governing the Harrison Memorial Fund, the Selection Committee, consisting of the Presidents of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the Pharmaceutical Society, will, after December 1st, 1956, consider making an award of the Harrison Memorial Prize.

The Prize, not exceeding 100 Guineas, will be awarded to the chemist of either sex, being a natural-born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, shall, during the previous five years, have conducted the most meritorious and promising original investigations in Chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should give the name of the applicant (in full); age (birth certificate should accompany the application); degrees (with name of University); any other qualifications and experience; tiltes of published papers (with co-authors' names) including full references to publication; where research was carried out; testimonials and references, and any other particulars bearing on the application.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates eligible for the Prize. Any such communication must be received by the President, The Chemical Society, Burlington House, Piccadilly, London, W.1, not later than Saturday, December 1st, 1956. Candidates must not have attained the age of thirty years at this date.

CORDAY-MORGAN MEDAL AND PRIZE.

This Award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 are due before the end of 1957.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in November next. All persons who have received grants, and whose accounts have not been declared closed by the Council, are informed that reports must be received by the Society not later than November 1st, 1956.

Applications for grants, to be made on forms available from the General Secretary, must be received on or before November 15th, 1956. Applications from Fellows will receive prior consideration.

Attention is drawn to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is principally devoted to the encouragement of research in inorganic and metallurgical chemistry and that the income from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

MR. JOHN CLARKE.

Mr. John Clarke, Commissionaire with the Society since 1926, retired at the end of April and, to mark the occasion, the President, on behalf of the Society, presented him with a watch.

DYERS' ESSAY COMPETITION.

To mark the centenary of W. H. Perkin's discovery of the first coal-tar dyestuff, the London Section of the Society of Dyers and Colourists is offering a prize of twenty-five guineas, an anonymous gift by a member of that Society, for the best essay on "The Influence of Perkin's Discovery, and of the Synthetic Dyestuffs which followed it, on any trade of the candidate's choice." Competitors need not be members of the Society of Dyers and Colourists, but they must live, work, or study in the area covered by the Society's London Section, which is South of a line joining Great Yarmouth and Gloucester. They must not have reached the age of twenty-six years on December 31st, 1956. Full details can be obtained from the Honorary Secretary of the Section, Mr. H. W. Taylor, 10, Milton Avenue, Sutton, Surrey.

SECOND INTERNATIONAL CONGRESS OF SURFACE ACTIVITY.

This Congress will be held in London from April 8th to 12th, 1957, with Lord Brabazon of Tara as the President of Honour and Sir Eric Rideal as the President.

An Organizing Committee has been set up under the Chairmanship of Dr. Leslie H. Lampitt, with Sir Charles Dodds as Honorary Treasurer and Lt.-Colonel Francis J. Griffin as Honorary Secretary.

Membership of the Congress is open to all interested persons on payment of the membership fee of £4. It is hoped to issue a detailed programme in the near future, and all enquiries should be addressed to the Honorary Secretary, IInd International Congress of Surface Activity 14, Belgrave Square, London, S.W.1.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held in the Great Hall of the University of Nottingham on Monday, March 26th, 1956, at 9.30 a.m.

The President, PROFESSOR W. WARDLAW, C.B.E., D.Sc., F.R.I.C., was in the Chair.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: G. G. F. Newton, Ronald Breslow, Eric Bullock, Julian E. Davies, E. J. Forbes, P. C. Jocelyn, Jas. L. Lowe, R. B. Arnold, P. G. Philpott, R. J. Moss, Peter R. Leeming, D. D. Chapman, Gordon Read, K. Elliott, K. G. Lewis, R. Massy-Westropp, W. C. Howell, J. T. Braunholtz, S. A. Warsi, D. M. Brasher, P. E. Macey, L. McGrath, J. P. Brown.

SYMPOSIUM.

The President called upon Professor A. W. Johnson to take the Chair for the morning session of the Symposium entitled "Antibiotics and Mould Metabolites." Professor Johnson welcomed the Society to the University of Nottingham and opened the Symposium. The following contributions were then made and discussed:

1. "Fungal Quinones," by J. H. Birkinshaw (London School of Hygiene and Tropical Medicine).
2. "Synthesis of some Fungal Metabolites," by D. H. R. Barton (University of Glasgow).
3. "Azophilones, a General Survey," by A. D. G. Powell, Alexander Robertson, and W. B. Whalley (University of Liverpool).
4. "The Structure of Purpurogenone," by J. C. Roberts (University of Nottingham).

The Symposium was resumed after lunch, with Professor E. R. H. Jones in the Chair. The following contributions were made and discussed:

5. "The Chemistry of Terramycin and Related Antibiotics," by L. H. Conover (Charles Pfizer and Co., U.S.A.).
6. "Actinomycin," by A. W. Johnson (University of Nottingham).
7. "Chemistry of the Cephalosporins," by E. P. Abraham and G. G. F. Newton (University of Oxford).

At the end of the Symposium the Chairman expressed the thanks of the Society to the contributors.

Minutes of a

SCIENTIFIC MEETING

held in the Great Hall of the University of Nottingham on Wednesday, March 28th, 1956, at 11 a.m.

The President, PROFESSOR W. WARDLAW, C.B.E., D.Sc., F.R.I.C., was in the Chair.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: F. C. Laxton, R. J. High, R. Michaelis, B. D. Shaw.

FARADAY LECTURE.

The President called upon Professor Dr. Otto Hahn to deliver the Faraday Lecture entitled " Personal Reminiscences of a Radiochemist." At the conclusion of the Lecture the President presented the Faraday Medal to Professor Dr. Hahn and proposed a vote of thanks to him for his lecture, which was carried with acclamation.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the Journal *for May, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Aroney, Manuel, M.Sc. (Sydney). British. Chemistry Department, Sydney University, Sydney, New South Wales, Australia. Teaching Fellow. *Signed by:* R. J. W. Le Fèvre, D. P. Craig.

Blackman, Lionel Cyril Francis, B.Sc. & Ph.D. (Lond.). British. 163, Tany's Dell, Harlow, Essex. Scientific Officer (Admiralty). *Signed by:* M. J. S. Dewar, W. J. Hickinbottom.

Blaker, John Warren, B.S. (Wilkes College). American. The Graduate House, Massachusetts Institute of Technology, Cambridge 39, Mass., U.S.A. Graduate Student. *Signed by:* H. O. House, A. C. Cope.

Broomhead, John Arthur, B.Sc. (Sydney). Australian. 13, Bell Street, Watsons Bay, Sydney, New South Wales, Australia. Student at Sydney University. *Signed by:* R. J. W. Le Fèvre, T. Iredale.

Cook, Reginald William Kell. British. 239, Marsh Lane, Preston, Lancs. Student. *Signed by:* W. J. Hickinbottom, R. F. Garwood.

Crawford, John Michael. Australian. Ormond College, University of Melbourne, Carlton, N.3, Victoria, Australia. Student. *Signed by:* K. H. Pausacker, J. G. Scroggie.

Cremlyn, Richard James William Campbell-Davys, B.Sc. and Ph.D. (Wales). British. Flat 5, Park Lodge, Binfield, Berks. Research Chemist with the Central Agricultural Control of I.C.I. Ltd., Bracknell. *Signed by:* G. W. Kenner, C. W. Shoppee.

Galt, Ronald Hilson Begg, B.Sc. (Glas.). British. Machany, Auchenlodment Road, Johnstone, Renfrewshire. Research Student at Glasgow University. *Signed by:* D. H. R. Barton, J. D. Loudon.

Gibson, Ian Hampson. Australian. 6, Delia Street, South Oakleigh, S.E.13, Victoria, Australia. Student at Melbourne University. *Signed by:* K. H. Pausacker, J. F. Duncan.

Gould, Patrick, B.Sc. (Lond.). British. 722, Fulham Road, London, S.W.6. Research Chemist. *Signed by:* F. R. Goss, J. A. Reid.

Karelsky, Margarita, B.Sc. (Melbourne). British. 6, Devon Road, Pascoe Vale, Victoria, Australia. Research Student *Signed by:* K. H. Pausacker, A. R. Fox.

Kimber, Ronald Walter Lincoln, B.Sc. (Adelaide). Australian. 45, Second Avenue, Forestville, Adelaide, South Australia. Student at Adelaide University. *Signed by:* G. M. Badger, P. R. Jefferies.

Kowanko, Nicholas, B.Sc. (Adelaide). Australian. 8, Duke Street, Beulah Park, South Australia. Student Teacher. *Signed by:* G. M. Badger, J. W. Clark-Lewis.

Leach, Reuben Sydney, B.Sc. (Lond.), D.-ès-Sc. (Paris). British. Laboratoire de Chimie-Physique, Faculté des Sciences de l'Université de Paris, 11, rue Pierre Curie, Paris 5e, France. Research Fellow of the French National Scientific Research Centre. *Signed by:* J. Sutton, C. M. Moser.

Okolski, Zbigniew Jan, B.Sc. (U.D.C.). Polish. c/o 116, Kennington Park Road, London, S.E.11. Chemist at The Counties Public Health Laboratories, S.W.1. *Signed by:* R. C. Hoather, D. A. Brown.

Priest, David Charles, B.A. (Coe College). American. Box 167, Department of Chemistry, University of N. Carolina, Chapel Hill, North Carolina, U.S.A. Student. *Signed by:* D. B. Bright, J. Bunnett.

Russell, Douglas William, B.Pharm. (Lond.) F.P.S. British. 53, Rosemary Road, London, S.E.15. Biochemical Research. *Signed by:* D. W. Mathieson, D. F. Elliott.

Simon, Sidney Frank, B.Sc. (Brooklyn Coll.). American. 44, Tavistock Square, London, W.C.1. Student at Birkbeck College, London. *Signed by:* R. C. Cookson, A. K. Chatterjee.

Sinclair, Lynne, A.R.I.C. British. 1, Upper Addison Gardens, London, W.14. Assistant Analyst. *Signed by:* S. G. E. Stevens, A. H. J. Cross.

Taylor, Nigel Hardy. British. 727, City Road, Manor, Sheffield, 2. Student at Oxford University. *Signed by:* L. A. K. Staveley, J. W. Linnett.

Ullman, Edwin F., B.A. (Reed Coll.), M.A. and Ph.D. (Harvard). American. American Cyanamid Company, Stamford, Connecticut, U.S.A. Research Chemist. *Signed by:* R. W. Young, S. B. Davis, G. W. Anderson.

Walton, Alan George. British. 39, Old Oak Road, Kings Norton, Birmingham, 30. Student at Nottingham University. *Signed by:* C. C. Addison, S. C. Wallwork.

Williams, Alan John, B.Sc. (Sydney). British. 18, Kissing Point Road, Turramurra, New South Wales, Australia. Student. *Signed by:* R. J. W. Le Fèvre, D. P. Craig.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Avasthi, Bal Krishna, M.Sc. and D.Phil. (Allahabad). Indian. Collège Néerlandais, 61, Boulevard Jourdan, Cité Universitaire, Paris, XIVE, France. Research work at the Pasteur Institute. *Signed by:* P. Verma.

Bagli, Jehanbux Framroz, B.Sc.Tech. (Bombay), Ph.D. (Lond.). Indian. Chemistry Department, Johns Jopkins University, Baltimore 18, Maryland, U.S.A. Research Associate. *Signed by:* A. Nickon.

Dunkel, Morris, B.S. (Long Island), M.A. (Brooklyn Coll.), Ph.D. (Arkansas). American. 1948—66 Street, Brooklyn 4, N.Y., U.S.A. Research Chemist. *Signed by:* J. Feltzin.

Hartman, George Solomon, M.S. (Lehigh). American. The Electric Storage Battery Company, P.O. Box 5723, Philadelphia 20, Pennsylvania, U.S.A. Assistant to the Director of Research. *Signed by:* C. C. Wallace.

Swaminathan, Sambasiva, M.A. (Annamalai), Ph.D. (Illinois). Indian. A. C. College, Madras-25, India. Reader in Organic Chemistry. *Signed by:* G. Eglinton.

Tinker, Philip Bernard Hague, B.Sc. and Ph.D. (Sheffield). British. West African Institute for Oil Palm Research, Benin, Nigeria. Research Chemist. *Signed by:* W. D. Walsh.

PAPERS ACCEPTED

(List of papers received between March 22nd and April 17th, 1956, for publication in the *Journal*).

" Hydrogen evolution at electrodeposited copper in hydrochloric acid." By (the late) S. E. S. El Wakkad, I. A. Ammar, and H. Sabry.

" Compounds of potential pharmacological interest. Part I. 3-Phenyl-1-indanamines." By R. M. Acheson, P. G. Philpott, K. E. MacPhee, J. S. Hunt, and J. A. Barltrop.

" The pinacol–pinacone rearrangement. Part I. Catalysis by strong monobasic acids." By J. F. Duncan and K. R. Lynn.

" The pinacol–pinacone rearrangement. Part II. Catalysis by sulphuric acid." By J. F. Duncan and K. R. Lynn.

" The pinacol–pinacone rearrangement. Part III. Evidence on general acid catalysis." By J. F. Duncan and K. R. Lynn.

" Synthesis of thionaphthen derivatives. Part I. The cyclisation of arylthioacetaldehyde diethyl acetals." By J. E. Banfield, W. Davies, and S. Middleton.

" Reactions of disodium pentacyanoamminoferrate with aromatic amines. Part I. The preparation and properties of compounds containing the pentacyano-*p*-hydroxyanilinoferrate ion." By E. F. G. Herington.

" Some aspects of the system uranium trioxide–water." By J. K. Dawson, E. Wait, K. Alcock, and D. R. Chilton.

" Manganese dioxide oxidation of some unsaturated carbinols." By K. R. Bharucha.

" Butadienes and related compounds. Part III. A study of the mechanism of formation of 1 : 1 : 4 : 4-tetrarylbuta-1 : 3-dienes." By Wadie Tadros, Alfy B. Sakla, and Youssef Akhnookh.

" Infrared spectra and polar effects. Part III. Internal spectral relationships." By L. J. Bellamy and R. L. Williams.

" The solubility of tungsten trioxide in hydrochloric acid." By (the late) S. E. S. El Wakkad and H. A. M. Rizk.

" Proof of the structure of ' D-glucosazone-formazan ' (1-phenylazo-D-glucosazone) by synthesis." By L. Mester and A. Major.

" New-type carbohydrate formazans." By L. Mester and E. Moczar.

" Tropolones. Part IX. 2 : 3-Dihydro-2 : 3-methylene-1 : 4-naphthaquinone." By G. L. Buchanan and J. K. Sutherland.

" Perfluoroalkyl derivatives of nitrogen. Part III. Heptafluoronitrosopropane, perfluoro-2-*n*-propyl-1 : 2-oxazetidine, perfluoro(methylene-*n*-propylamine), and related compounds." By D. A. Barr and R. N. Haszeldine.

" Isolation and properties of pure actinomycins." By G. G. Roussos and L. C. Vining.

" An infrared spectroscopic investigation of absorption due to the N–H stretching modes of vibration in co-ordination compounds of ammonia and amines. Hydrogen bonding (N–H . . . Cl) in a series of amine complexes of platinous chloride." By J. Chatt, L. A. Duncanson, and L. M. Venanzi.

" The spectra of some solid cobaltic nitroammines, and certain other cobaltic complexes, in the 2—15 μ region." By I. R. Beattie and H. J. V. Tyrrell.

" Mechanism, kinetics, and stereochemistry of octahedral substitutions. Part VI. Bimolecular basic hydrolysis and aquation of the chloronitrobis(ethylenediamine)cobalt(III) ions." By S. Ašperger and C. K. Ingold.

" Glycine peptides. Part III. The absorption of Orange II by polyglycine." By A. B. Meggy and D. Sims.

" The chemistry of triterpenes and related compounds. Part XXVIII. β-Boswellic acid." By J. L. Beton, T. G. Halsall, and E. R. H. Jones.

" The use of deactivated charcoals for the isolation of aromatic substances." By A. Asatoor and C. E. Dalgliesh.

" Studies of the strength of poison-to-catalyst bonds. Part I Heats of adsorption of ethyl sulphide and thiophen on platinum." By E. B. Maxted and M. Josephs.

" The chemistry of the transition elements. Part II. Some carbonyl compounds of ruthenium." By R. J. Irving.

" Double melting of molecular addition compounds of dinitrogen tetroxide with organic donors." By C. C. Addison and J. C. Sheldon.

" The ionisation functions of cyanoacetic acid in relation to the structure of water and the hydration of ions and molecules." By F. S. Feates and D. J. G. Ives.

" The pyrolysis of chloroalkenes. Part III. The molecular mode of decomposition of the 1 : 2-dichloroethylenes." By (Miss) A. M. Goodall and K. E. Howlett.

" The micro-flame detector in gas–liquid partition chromatography—correlation of response with heats of combustion." By J. I. Henderson and J. H. Knox.

" Some reactions of scandium." By R. C. Vickery.

" A synthesis of 3 : 4-benzopyrene-1 : 5-quinone." By R. O. C. Norman and William A. Waters.

" A thermochemical evaluation of bond strengths in some carbon compounds. Part IV. Bond-strength differences based on the reaction : $RI + HI \longrightarrow RH + I_2$, where R = *p*-methoxyphenyl and *cyclo*hexyl." By D. Brennan and A. R. Ubbelohde.

" Polynuclear heterocyclic systems. Part X. The Elbs reaction with heterocyclic ketones." By G. M. Badger and B. J. Christie.

" Decarboxylative acylations with α-aminophenylacetic acid." By Alexander Lawson.

" The auxochromic effect of the *cyclo*butane ring." By J. J. Wren.

" Polypeptides. Part II. The preparation of some protected peptides of cysteine and glycine." By K. C. Hooper, H. N. Rydon, J. A. Schofield, and (in part) G. S. Heaton.

" Polypeptides. Part III. The oxidation of some peptides of cysteine and glycine." By G. S. Heaton, H. N. Rydon, and J. A. Schofield.

" The reaction of dialkyl sulphites with sodium iodide in acetone." By A. B. Foster, E. B. Hancock, W. G. Overend, and J. C. Robb.

" Synthetic chabazites : correlation between isomorphous replacements, stability, and sorption capacity." By R. M. Barrer and J. W. Baynham.

" Benzo[*a*]perylene and derivatives." By E. Clar, W. Kelly, D. G. Stewart, and (in part) J. W. Wright.

" The synthesis of 1 : 2-dihydro-1-oxo-5′-phenylfurano(2′ : 3′-3 : 4)*iso*quinoline." By A. S. Bailey and D. L. Swallow.

" The rearrangement of ketones containing tertiary alkyl groups." By S. Barton and C. R. Porter.

" The S_N mechanism in aromatic compounds. Part XIX." By R. L. Heppolette and Joseph Miller.

" Oxidation of organic sulphides. Part VII. The mechanism of autoxidation of but-2-enyl methyl sulphide, methyl 1-methylbut-2-enyl sulphide, and *n*-butyl methyl sulphide." By L. BATEMAN, J. I. CUNNEEN, and J. FORD.

" The structure of cyperone. Part V. The steric course of reduction of the cyperones." By R. HOWE and F. J. MCQUILLIN.

" Addition reactions of heterocyclic compounds. Part III. 2 : 3-Benzacridine and some dienophiles." By R. M. ACHESON and C. W. JEFFORD.

" Critical concentrations of some alkylpyridinium iodides in water and in xylene evaluated from solubility measurements." By C. C. ADDISON and C. G. L. FURMIDGE.

" Thiadiazoles. Part III. 3-Amino-5-arylamino- and 3 : 5-di(aralkylamino)-1 : 2 : 4-thiadiazoles." By FREDERICK KURZER.

" The Friedel–Crafts reaction in the carbazole series. Part V." By D. G. BROOKE and (the late) S. G. P. PLANT.

" Infrared spectra and structure of some quinone monoximes." By D. HADŽI.

" Phosphorylation through glyoxalines (iminazoles) and its significance in enzymic transphosphorylation." By J. BADDILEY, J. G. BUCHANAN, and R. LETTERS.

" Carcinogenic nitrogen compounds. Part XX. Benzacridines, benzocarbazoles, and benzophenarsazines with hydrogenated rings." By NG. PH. BUU-HOÏ, PIERRE JACQUIGNON, and DENISE LAVIT.

" A synthesis of (±)-pulegone." By C. BLACK, G. L. BUCHANAN, and (MISS) A. W. JARVIE.

" Aryldihydroresorcinols. Part I. Dihydro-5-α-naphthyl- and 5-(4-diphenyl)dihydroresorcinols." By E. E. AYLING, (the late) J. HODGES, and R. F. K. MEREDITH.

" The preparation and properties of some plutonium compounds. Part IV. Crystalline plutonium nitrate." By J. L. DRUMMOND and G. A. WELCH.

" The infrared spectra of some metal ammines and deuteroammines." By D. B. POWELL and N. SHEPPARD.

" Perfluoroalkyl derivatives of sulphur. Part V. αα-Difluoro-α-(trifluorothio)acetic acid." By R. N. HASZELDINE and F. NYMAN.

" Trinuclear dyes related to oxonols. Part II. Formation and absorption spectra." By R. A. JEFFREYS.

" A study of oxidation of monohydric phenols by alkaline ferricyanide." By C. G. HAYNES, A. H. TURNER, and WILLIAM A. WATERS.

" The formation of borate complexes by hydroxamic acids." By A. L. GREEN.

" Synthesis of all-*trans*-, 2-*cis*-(or *neo*-), and 6-*cis*-[2-^{14}C]vitamin A." By C. F. GARBERS.

" Chemical studies in the biosynthesis of purine nucleotides. Part I. The preparation of *N*-glycylglycosylamines." By J. BADDILEY, J. G. BUCHANAN, R. E. HANDSCHUMACHER, and J. F. PRESCOTT.

" The diffusion in water of some association colloids and solubilised materials." By N. BRUDNEY and L. SAUNDERS.

" 8-Mercaptoquinoline." By G. M. BADGER and R. G. BUTTERY.

" *Aconitum* and *Delphinium* alkaloids. Part I. The environment of the nitrogen atom in delpheline." By R. C. COOKSON and M. E. TREVETT.

" The reduction of β-alkylnaphthalenes." By A. S. BAILEY, J. C. SMITH, and C. M. STAVELEY.

" Ribose and its derivatives. Part VII. The condensation of methyl D-ribopyranoside with acetone." By G. R. BARKER and J. W. SPOORS.

" Hydrolysis of aryl sulphonates. Part II. Kinetic form of hydrolysis." By C. A. BUNTON and V. A. WELCH.

" Pyrimidine reactions. Part I. Pyrimidines from malondiamide." By D. J. BROWN.

" Organic fluorine compounds. Part IV. Some reactions of difluoromalonyl chloride and the action of iodine on disilver difluoromalonate." By E. J. P. FEAR, J. THROWER, and J. VEITCH.

" Diazepines. Part I. Condensation of acetylacetone with 1 : 2-diamines." By DOUGLAS LLOYD and DONALD R. MARSHALL.

" Reaction-kinetic investigations of the incomplete dissociation of salts. Part IV. The neutralization of nitroethane by solutions of metallic hydroxides." By R. P. BELL and M. H. PANCKHURST.

ADDITIONS TO THE LIBRARY

Physical chemistry, by N. K. Adam. Clarendon Press. 1956. (Presented by the Author.)

Advances in protein chemistry, edited by M. L. Anson, K. Bailey, and J. T. Edsall. Vol. 10. Academic Press Inc. 1955.

The properties of aluminium and its alloys. (Aluminium Development Association Information Bulletin No. 2.) 4th edn. Aluminium Development Assoc. 1955. (Presented by the Publishers.)

Methods for determining lead in air and in biological materials, 2nd edn. American Public Health Association, Inc. 1955.

Proceedings of the fifth conference on chemical works safety, held at Harrogate, 1954. Association of British Chemical Manufacturers. 1955.

Official methods of analysis of the Association of Official Agricultural Chemists, edited by W. Horwitz, 8th edn. Association of Official Agricultural Chemists, Washington. 1955.

Food technology processing and laboratory control, edited by F. Aylward. (Chemical and Chemical Engineering Series.) George Newnes, Ltd. 1955. (Presented by the Editor.)

Introduction to chemical engineering, by W. L. Badger and J. T. Banchero. McGraw-Hill Book Company, Inc. 1955.

Memorial Number to Sir Edward Mellanby. Recent Research on Vitamins. *British Medical Bulletin*, 1956, Vol. 12, No. 1. British Council Medical Department. 1956.

Paint and varnish manufacture, edited by H. W. Chatfield. (Chemical and Chemical Engineering Series.) George Newnes, Ltd. 1955. (Presented by Dr. T. H. Morton.)

Elsevier's Encyclopædia of Organic Chemistry, edited by F. Radt. Series III (carboisocyclic condensed compounds), Vol. 14—supplement (Steroids), Part 2 (substituted monohydroxyl compounds, polyhydroxyl compounds), edited by A. Georg. Elsevier Publishing Company. 1956.

European Brewery Convention, Proceedings of the [fifth] congress, Baden-Baden, 1955. Elsevier Publishing Co. 1955.

Proceedings of the first international neurochemical symposium, held at Oxford, 1954. Biochemistry of the developing nervous system, edited by H. Waelsch. Academic Press, Inc. 1955.

Kinetic theory of liquids, by J. Frenkel. Dover Publications Inc. 1955. (Presented by the Publishers.)

Chemical trade names and chemical synonyms; a dictionary of American usage, by W. Haynes. 2nd edn. D. Van Nostrand Company, Inc. 1955.

Verteilungsverfahren im Laboratorium, by Dr. E. Hecker. (Monographien zu *Angewandte Chemie und Chemie-Ingenieur-Technik*, Nr. 67). Verlag Chemie, GMBH. 1955.

Handbook of chemistry and physics. A ready-reference book of chemical and physical data; edited by C. D. Hodgman, R. C. Weast, and S. M. Selby. 37th edn. Chemical Rubber Publishing Co. 1955. (Presented by the Publishers.)

Metallurgical thermochemistry, by O. Kubaschewski and E. Ll. Evans. 2nd edn. Pergamon Press, Ltd. 1956.

Physical chemistry. by W. J. Moore. 2nd edn. Longmans, Green and Co. 1956.

Spektrochemische Betriebsanalyse mit praktischen Ratschlägen für die ausführung spektrochemischer Analysen im Betriebslaboratorium, by H. Moritz. Die chemische Analyse. Vol. 43, 2nd edn. Ferdinand Enke Verlag.

Introductory quantitative chemistry, by A. R. Olson, C. W. Koch, and G. C. Pimentel. (A series of chemistry texts, edited by Linus Pauling.) W. H. Freeman and Co. 1956. (Presented by the Publishers.)

Chimia si tehnologia colorantilor azoici, by I. Reichel. Editura Academiei Republicii Populare Romine. 1955. (Presented by the Rumanian Academy of Sciences.)

Polymer processes; chemical technology of plastics, resins, rubbers, adhesives, and fibers, edited by C. E. Schildknecht. (High polymers, Vol. 10.) Interscience Publishers, Inc. 1956.

British scientific instruments, 1956. Directory and handbook of the Scientific Instrument Manufacturers Association of Great Britain, Limited. S.I.M.A. 1956. (Presented by the Publishers.)

Society of Biological Chemists, India, silver jubilee souvenir. The Society of Biological Chemists, India. 1955. (Presented by the Publishers.)

Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels, by J. S. Stas. (Extrait du tome XXXV des Mémoires de l'Académie royale des sciences, des lettres et des beaux-arts de Belgique, 1865.) l'Académie Royale de Belgique. 1865. (Presented by J. Vargas Eyre.)

Topley and Wilson's principles of bacteriology and immunity, by G. S. Wilson and A. A. Miles. 2 vols. 4th edn. Edward Arnold, Ltd. 1955.

The third dimension in chemistry, by A. F. Wells. Clarendon Press. 1956.

Resonance in organic chemistry, by G. W. Wheland. John Wiley & Sons. 1955.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	H. B. Henbest, Ph.D., A.R.C.S., A.R.I.C., Chemistry Department, The University, Manchester, 13.
,,	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
,,	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham.	C. C. Addison, D.Sc., Ph.D., F.R.I.C., Chemistry Department, The University, University Park, Nottingham.
Oxford.	L. A. K. Staveley, M.A., Inorganic Chemistry Laboratory, South Parks Road, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.
,,	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Pandurang Narajan Joshi (Bombay)	Jan. 18th, 1945.	Feb. 12th, 1956.
Arthur Landauer Stern (Chorley Wood)	Dec. 6th, 1888.	Apr. 26th, 1956.

ELECTION OF NEW FELLOWS.

The following 143 candidates were elected to the Fellowship on May 3rd, 1956:

Frank Abbey.
Joe Alfred Adamcik.
Janet Allinger.
Reinhard Richard Arndt.
John Arris.
Derek Wilfred Aubrey.
Abdul Latif Bacchus.
Neville John Baines.
George Baum.
Neville Ernest Bean.
Colin Charles Beard.
John Moody Beaton.
John Biggs.
Jannik Bjerrum.
Jean Winifred Brooks.
Anne Frances Brown.
Frank Brown.
Patricia Margaret Brown.
Stanley Sidney Brown.
Zdzislaw Jan Bujwid.
Leslie Bunfield.
Ian James Cantlon.
James Frederick Carson.
John Reginald Chase.
Anne Elizabeth Marie Chaplin.
John Shipley Clarke.
Richard Clarkson.
Joseph A. Cogliano.
Thomas William Corpe.
Kenneth Nelson Cross.
Arthur William Dawkins.
Henri Dietrich.
Kenneth Dixon.
Dennis Albert Dowden.
John Michael Francis Drake.
Phanindra Chandra Dutta.
Leonard Kenneth Dyall.
Thomas Elmezzi.
Arthur Raymond Gordon Emslie.
Arnold B. Finestone.
Cesare Finzi.
Carl Wilhelm Fischer.
Abdallah Mohamed Fleigel.
Gordon Foster.
James Fraser.
John Friend.
John Herbert Garside.
Edward William Gill.
Esmarch Senn Gilreath.
Terence George Goodburn.
Ian Kelvin Gregor.
Norman Francis Hardie.
Stephen Henry Harvey.
Edwin Haslam.
Hans Jorg Hediger.
John Richards Herbert.
Gordon Hetherington.
Ivan Andrew Holliday.
Joseph Simeon Howarth.
Andrew Walter Jackson.
Amolak Chand Jain.
Megh Kumar Jain.
Leslie Cyril Johnson.
Eric Johnston.
Vera Johnston.
William Arthur Jones.
Herbert C. Katz.
Fred Allan Kincl.
David Kirkaldy.
Ian Lauder.
Derek Robert Lawrance.
John David Lee.
Norman Logan.
Louis Long, jun.
George Harry Lord.
Robert Michael Lukes.
Denis James McCaldin.
Francis Joseph McGuire.
Phillip Pleydell Manning.
Peter James March.
Edward Markham.
Louis Marnef.
Elliot Nelson Marvell.
David Hugh Miles.
Alwin S. Milian, jun.
Theodore Mill.

Glyn Miller.
Robert Clay Miller.
Graeme Crocker Morris.
Peter Eric Geoffrey Moult.
William McClement Muir.
Brown Lewis Murr, jun.
C. Natarajan.
Robert Livingston Nelson.
Eileen Dorothy Nickels.
Colm O hEocha.
Richard Vernon Parish.
Cumming Paton.
Albert Peter Paul.
Geoffrey Howard Pickerell.
Peter Jules Pinot de Moira.
Anthony Lloyd Price.
Charles C. Price.
Mohammed Hafizur Rahman.
John George Raphael.
Ronald Steven Ratney.
John Barrie Raynor.
Allen Forrest Reid.
William Henry Reusch.
Arnold Rosen.
Donald Malcolm Rowlingson.
Adib Salama.
Tahani Mahmoud Salem (Mrs.).
Roy Salter.
Hans Thomas Sanders.
John Marshall William Scott.
William Peter Scott.
Douglas Shooter.
Sydney Skidmore.
Keith Slater.
Barry Charles Smith.
Brian Carl Stace.
George M. Steinberg.
Edith Stephen.
John David Stevens.
Frederick Willem Stonner.
John Boris Taylor.
Pieter ten Haken.
Colin Reginald Thomas.
Daniel James Thomas.
Lydia Vallarino.
André von Bezard.
Richard Bernard Ward.
Ernest William Thomas Warford.
David Neil Waters.
John Michael Webber.
Karl H. Weiss.
Ian Wellings.
Raymond James Withey.
Patricia Maureen Woodhams.
John Douglas Michael Wraige.
Alexander Neil Wright.
Alfred Zeller.

SCIENTIFIC MEETINGS.

The following dates of Scientific Meetings during the Session 1956—1957 have been approved by Council:

1956.	1957.
Thursday, October 18th	Thursday, January 17th
,, November 1st	,, February 14th
,, November 15th	,, February 28th
,, December 13th	,, March 14th
	,, May 9th
	,, June 6th

The Anniversary Meetings will be held in Cambridge from April 10th to 12th, 1957.

LIBRARY.

From July 16th until September 30th, 1956, the Library will close at 5 p.m. instead of 7.30 p.m., and it will not be open on August 6th and 7th, 1956.

PROCEEDINGS OF THE CHEMICAL SOCIETY, 1957.

Council has approved plans for a change in the style, format, and contents of the Society's *Proceedings*. From January, 1957, *Proceedings* will be considerably increased in size by the inclusion of additional material which it is hoped will add greatly to the interest and permanent value of the publication. The new *Proceedings* will be given without extra charge to all Fellows who have paid the basic annual subscription, or who are Life Fellows, and to all non-Fellows subscribing to the *Journal*. In addition, non-Fellows may, if they wish, subscribe separately to *Proceedings*.

In its new form *Proceedings* will no longer be issued as an insert in the *Journal*, but it will have its own distinctive cover, and will be printed in Times New Roman type on a white paper, thicker in substance than the tinted paper at present used. It will include lectures and obituary notices, and the Report of Council, which now appear in the *Journal*. It will also contain occasional articles, anonymous or signed, and personal news items concerning distinguished Fellows and visitors from overseas, as well as other news items

of general interest, and the official announcements which already appear. Reports of Scientific Meetings held by the Society will be included, as well as short scientific "Communications" which are sufficiently urgent or important to qualify for the accelerated publication and the greatly increased circulation that *Proceedings* will offer by comparison with the *Journal*. Notes regarding the submission of "communications" are given below. It is also expected that *Proceedings* will include, in addition to the advertisements at present printed in the *Journal*, a section of classified small advertisements, including notices of appointments vacant, etc.

Considerably less than half the total Fellowship now receives the *Journal*, and *Proceedings* is, therefore, the only regular link which the Society has with many of its Fellows. The Council hopes that the improvements which are now planned will be welcomed by Fellows and by non-Fellows alike, and that they will form an attraction to prospective Fellows, and also will help to retain the interest of those Fellows who no longer need to subscribe to the Society's *Journal*.

"COMMUNICATIONS" FOR PROCEEDINGS, 1957.

Starting in January 1957, *Proceedings of the Chemical Society* will be open to "Communications" which deal with original work of immediate importance to a substantial body of chemists. (See previous item.) Publication will be granted only to "Communications" which satisfy each of these three requirements, *i.e.*, urgency, importance, and wide interest. The primary consideration will be that chemists in general shall benefit from information in advance of full publication. The object shall be to share knowledge, not to claim priority or reserve a field. Polemics, including prolonged argument about known experimental facts, would not be acceptable.

Details of experimental methods will not be published unless they are an essential part of the "Communication," nor will the physical or chemical properties of intermediates in syntheses or degradations.

"Communications" will be considered for publication whether or not the author is a Fellow of the Chemical Society. They will be subject to refereeing, and, if accepted, to editing. Authors are advised to submit, with the manuscript, a statement for the benefit of referees setting out briefly the reasons why publication in advance of full presentation is requested.

Authors whose "Communications" are accepted should consider themselves under obligation to publish adequate details as soon as possible, or to withdraw the claims made, but not necessarily in a publication of the Chemical Society.

Manuscripts must be marked "Communication for Proceedings" and sent, in duplicate, to the Honorary Secretaries, The Chemical Society, Burlington House, Piccadilly, London, W.1. They should not normally exceed 600 words in length, *i.e.*, 3 quarto pages in double-line spacing, including formulæ or diagrams, which should be kept to a minimum and may delay publication. It is hoped that accepted "Communications" will be published within 4—8 weeks of receipt. It is unlikely, however, that manuscripts received after December 18th, 1956, will be included in the first issue.

Authors should observe the Society's conventions for nomenclature, symbolism, etc., outlined in the brochure "The Presentation of Papers for the Journal of the Chemical Society," but references should be given as footnotes (see *Proceedings of the Chemical Society*, July 1955, pp. 79—81.)

CORDAY-MORGAN MEMORIAL FUND EXECUTIVE.

The Executive has appointed Dr. M. Lamchen, Senior Lecturer in Chemistry, University of Cape Town, Rondebosch, Cape Town, South Africa, as the Corday-Morgan Commonwealth Fellow for 1956—1957. Dr. Lamchen is to carry out a year's research work in the laboratories of Sir Alexander Todd at Cambridge.

The Executive has issued the following Report for the three years ended December 31st, 1955:

"The Executive was appointed in 1951 to administer grants made to it by The Chemical

Society from the Corday–Morgan Memorial Fund, or from other sources. In accordance with the purpose of the original bequest, the Executive has used the funds at its disposal to inaugurate the Corday–Morgan Commonwealth Fellowship.

" These Fellowships are intended to provide an opportunity for post-doctorate (or equivalent) study, and are tenable at any university or research establishment approved by the Executive in any part of the Commonwealth outside the home country of the Fellow appointed. The Fellowships are at present offered to any one country of the Commonwealth nominated each year by the Executive.

" Three appointments have so far been made, as follows :

1952—1953—Dr. H. J. Anderson (University of Manitoba, Canada).
Fellowship held at : The University of Oxford.
1953—1954—Dr. A. D. Campbell (University of Otago, New Zealand).
Fellowship held at : The University of Glasgow.
1954—1955—Dr. L. E. Smythe (University of Tasmania).
Fellowship held at : The University of Cambridge.

" The Executive wishes to record its thanks and appreciation for the assistance rendered in the countries concerned, where in each case a selection committee was appointed to advise the Executive concerning the appointments. No Fellowship was awarded for the year 1955—1956, but it is intended that the next award, for the year 1956—1957, shall be made to a graduate of a South African university.

" The Executive wishes to record its grateful thanks to the Chairman and Directors of Imperial Chemical Industries Ltd. for a donation of £300 to assist in the award of Fellowships."

VAN'T HOFF FUND.

The Committee of the Van't Hoff Fund for the endowment of investigations in the field of pure and applied chemistry invites applications for grants from the fund.

The amount available for 1957 is about 1600 Dutch guilders, and applications should be sent by registered post to Het Bestuur der Koninklijke Nederlandse Academie van Wetenscheppen, bestemd voor de Commissie van het " Van't Hoff Fonds," Trippenhuis, Kloveniersburgwal 29, Amsterdam, before November 1st, 1956. Applicants must state the amount of the grant desired and the purpose for which it is required.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at Burlington House on Thursday, May 3rd, 1956, at 7.30 p.m.

The President, Professor E. L. Hirst, M.A., D.Sc., F.R.S., was in the Chair.

MINUTES.

The minutes of the Scientific Meetings held at Burlington House on February 16th and at the University of Nottingham on March 26th and 28th, 1956, were taken as read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society : A. C. Riddiford, N. L. Paddock, C. J. L. Booker.

SCIENTIFIC COMMUNICATIONS.

The following papers were presented :

" Transport to the Surface of a Rotating Disc," by D. P. Gregory and A. C. Riddiford.

" On the Photodecomposition of Carbon Dioxide and of Ammonia by Xenon 1470Å Radiation," by H. Jucker and Sir Eric Rideal.

" The preparation of active solids by thermal decomposition. Part IX. The calcination of ferric oxide hydrate and of lepidocrocite," by J. F. Goodman and S. J. Gregg.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of the publication of the Journal *for June, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Axford, Thomas Ewart, B.Sc. (Madras). British. 25, King Edward Road, Oldfield Park, Bath, Somerset. Lecturer in Chemistry at City of Bath Technical College. *Signed by :* P. A. R. Freeman, A. J. H. Hamblin.

Bayer, Zdenek. Czech. Spol. dom, Svit-Tatry, Czechoslovakia. Research at the Institute of Artificial Fibres, Svit-Tatry. *Signed by :* J. Jelinek, M. Bil.

Bohny, Paul Emil, Ph.D. (Basle). Swiss. 134, Wigmore Street, London, W.1. Manager of Sandoz Products Ltd. *Signed by :* L. H. Lampitt, J. Walker.

Bush, Donald James, B.A. (Cantab.). British. 31, St. Charles Square, North Kensington, W.10. Senior Technician at the Postgraduate Medical School, W.12. *Signed by :* K. E. Howlett, C. E. Dalgliesh.

Cockburn, Bruce Lindsey, B.Sc. (Wellington). British. 22, Taft Street, Wellington, S.W.1., New Zealand. Student. *Signed by :* S. N. Slater, W. E. Dasent.

Collette, John Wilfred, B.Sc. (Alberta). Canadian. Chemistry Department, University of California, Berkeley, California, U.S.A. Teaching Assistant. *Signed by :* A. Streitwieser, W. G. Dauben.

Collett-Jones, Thomas, M.P.S. British. 30, High Street, Burnham, Bucks. Director. *Signed by :* H. H. Jones, P. W. C. Barnard.

Conte, John Salvatore, A.B. (La Salle College). American. Leahy and Anderson Avenue, Swedesboro, New Jersey, U.S.A. Student at Louisiana State University. *Signed by :* H. I. Stonehill, O. S. Pascual.

Corbett, Terence Guy, B.Sc. (Wellington). British. Weir House, Salamanca Road, Kelburn, Wellington, W.1., New Zealand. Student. *Signed by :* S. N. Slater, W. E. Dasent.

Cowper, Robert Munro, Ph.D. British. 14, Cowdray Crescent, Renfrew. Head of Research Laboratory, J. and P. Coats Ltd., Paisley. *Signed by :* R. M. Gailey, J. D. Loudon.

Crew, John Leonard. British. 81, Bolina Road, South Bermondsey, S.E.16. Lubrication Chemist. *Signed by :* M. Vahrman, R. F. Greenwood.

Dendy, David Albert Victor, B.Sc. (Liv.), A.R.I.C. British. 8, Sherburn Close, Barlow's Lane, Fazakerley, Liverpool 9. Research Student at Liverpool University. *Signed by :* A. Robertson, D. A. H. Taylor.

Di, Maung, B.Sc. (Rangoon). Burmese. 76, West Cromwell Road, London, S.W.5. Student at Imperial College. *Signed by :* B. Atkinson, M. M. Gale.

Eberson, Lennart Eugen. Swedish. Regementsgat 58, Malmö, Sweden. Research Assistant. *Signed by :* E. Larsson, S. Sunner.

Harper, David Augustine, Ph.D. (Liv.), F.R.I.C. British. Baldrand, Bowerham Road, Lancaster. Managing Director of Storey Brothers and Co. Ltd., White Cross, Lancaster. *Signed by :* M. A. T. Rogers, R. J. W. Reynolds.

Hertler, Walter R., A.B. (Pennsylvania). American. 47, Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A. Student. *Signed by :* D. Y. Curtin, R. W. White.

James, Frederick Charles, M.Sc. (Melbourne). British. 66, Laurel Grove, Blackburn South, Victoria, Australia. Lecturer in Organic Chemistry, Royal Melbourne Technical College. *Signed by :* K. H. Pausacker, P. F. Nelson.

Lawler, James Joseph, B.Sc. (U.C.D.), A.R.I.C. Irish. 336, Lordship Lane, East Dulwich, S.E.22. Lecturer in Chemistry at East Ham Technical College. *Signed by :* P. L. Wyvill, L. J. Couzens.

Lebel, Norman Albert, A.B. (Bowdoin College). American. 332, Westgate West, Cambridge 39, Massachusetts, U.S.A. Student at Massachusetts Institute of Technology. *Signed by :* A. C. Cope, F. D. Greene.

Matheson, Norman Keith, M.Sc. (Sydney), Ph.D. (Edin.). British. Chemistry Department, Queen's University, Kingston, Ontario, Canada. Post-Doctorate Fellow. *Signed by :* J. K. N. Jones, K. E. Russell.

Nauta, Wybe Thomas. Dutch. Looiersgracht 27—39, Amsterdam-C, Holland. Professor of Organic and Medicinal Chemistry, Vrije Universiteit, Amsterdam. *Signed by :* J. Coops, J. P. Wibaut.

Nield, Eric, B.Sc. (Birm.). **British.** Chemistry Department, The University, Edgbaston, Birmingham 15. Research Student. *Signed by:* J. C. Tatlow, G. Fuller.

Oldham, Kenneth Gordon, B.Sc. (Lond.). British. 10, Queen's Avenue, Finchley, N.3. Student at University College, London. *Signed by:* P. W. C. Barnard, C. A. Bunton.

Olliff, Raymond Walter, M.Sc. (New Zealand). British. 2, Abbey Street, Auckland, C.2, New Zealand. Lecturer in Chemistry at Auckland University College. *Signed by:* F. J. Llewellyn, L. H. Briggs.

Pope, Gerald Seaton, B.Sc. (Reading), D.Phil. (Oxon.), A.R.I.C. British. 19, Westlands Avenue, Shinfield, Reading. Research Chemist. *Signed by:* H. D. Kay, A. W. Marsden.

Redfern, John Priestnall, B.Sc. (Lond.), A.R.I.C. British. 35, Nimrod Road, London, S.W.16. Lecturer in Inorganic Chemistry at Battersea Polytechnic. *Signed by:* J. E. Salmon, J. Genge.

Rosenberg, Arthur Stanley, B.S. (Vermont). American. 47, Park Vale Avenue, Allston 34, Massachusetts, U.S.A. Student. *Signed by:* T. E. C. Knee, C. G. Swain.

Rosenblum, Myron, A.B. (Columbia), A.M. and Ph.D. (Harvard). American. Department of Chemistry, Illinois Institute of Technology, Chicago 16, Illinois, U.S.A. Teacher. *Signed by:* R. Filler, M. L. Bender.

Satchell, Derek Peter Norman, Ph.D. (Lond.). British. 51, Brancaster Road, Purley, Surrey. Assistant Lecturer in Chemistry at King's College. *Signed by:* I. R. Beattie, N. D. Weston.

Smolinsky, Gerald, B.S. (Drexel Inst. of Technology). American. Department of Chemistry, University of California, Berkeley 4, California, U.S.A. Student. *Signed by:* A. Streitwieser, D. S. Noyce.

Summers, Lindsay Anderson, Ph.D. (Glas.). British. c/o Richmond, 38, Caledonia Road, Saltcoats, Ayrshire. Research Chemist with I.C.I. Ltd., Nobel Division, Stevenston. *Signed by:* J. Peters, B. W. Pengilly.

Veale, Colin Ronald, Ph.D. (Lond.), A.R.C.S., D.I.C., A.R.I.C. British. 37, Eastmont Road, Esher, Surrey. Research Chemist. *Signed by:* G. R. Davies, N. E. Topp.

Wall, Richard Arthur, A.B. (California), Ph.D. (Edin.). American. 20, Jane Street, Apartment 3B, New York 14, New York, U.S.A. Chemist with U.S. Army. *Signed by:* K. C. B. Wilkie, J. K. N. Jones.

Ward, Peter George. British. 195, Britannia Road, Ipswich, Suffolk. Medical Research Technician with the Human Nutrition Research Unit. *Signed by:* D. J. G. Ives, W. Wardlaw.

Weitzman, Peter David Jacob. British. 19, Amesbury Crescent, Hove, Sussex. Undergraduate at Oriel College, Oxford. *Signed by:* L. A. K. Staveley, B. R. Brown.

Woods, Mervyn Charles, B.Sc. (Western Australia). Australian. 89, Mabel Street, North Perth, Western Australia. Student at University of Western Australia. *Signed by:* D. E. White, R. L. Heppolette.

Zollinger, Heinrich, D.Sc. (Zurich). Swiss. 9, Im Marteli, Binningen, Switzerland. Research Chemist with Ciba Ltd., Basle. *Signed by:* C. K. Ingold, E. D. Hughes.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Ahmad, S. Shahabuddin, M.Sc. (Patna). Pakistani. Department of Chemistry, Rajshahi University, Rajshahi, East Pakistan. Lecturer in Chemistry. *Signed by:* M. I. D. Chughtai.

Dun, Alan. British. University of New England, Armidale, N.S.W., Australia. Demonstrator. *Signed by:* N. V. Riggs.

PAPERS ACCEPTED

(List of Papers accepted between April 19th and May 17th, 1956, for publication in the *Journal*.)

"The polarographic reduction of xanthone and methoxyxanthones." By W. E. Whitman and L. A. Wiles.

"Studies on the aloins. Part I. The structure of barbaloin." By J. Evelyn Hay and L. J. Haynes.

"Synthesis in the quinazolone series. Part II. Synthesis of quino- and quinazoquinazolones." By Theodora Stephen and Henry Stephen.

"Syntheses in the quinazolone series. Part III. The formation of quinazo[4 : 3-*b*]quinazol-8-one and 2-*o*-aminophenylquinazol-4-one during the preparation of 4-chloroquinazoline." By Theodora Stephen and Henry Stephen.

"Kinetics and mechanism of hydrochlorination of the surface of rubber latex particles." By Manfred Gordon and Thomas Carbarns.

"Preparation, stability, and complex formation of aryloxyboron compounds." By T. Colclough, W. Gerrard, and M. F. Lappert.

"Ion-exchange studies of solutions of borates." By D. A. Everest and W. J. Popiel.

" Molecular polarisability. The C–C, C–O, C=O, C–Cl, C–Br, and C–I link polarisabilities, and the conformations of *cyclo*pentane, of *cyclo*hexyl chloride, bromide, and iodide, of *cyclo*pentanone, *cyclo*hexanone, *cyclo*hexane-1 : 4-dione, camphor, paraldehyde, and tetrahydrofuran." By (Mrs.) C. G. Le Fèvre and R. J. W. Le Fèvre.

" The crystal structure of dimethylketen dimer." By P. H. Friedlander and J. Monteath Robertson.

" Interaction of acetyl peroxide with but-3-enoic acid and crotonic acid. A new example of allylic shift of olefinic bond in free radical reactions." By K. B. L. Mathur and R. S. Thakur.

" E.m.f. measurements in acetone–water mixtures: the cell H_2(Pt)|HCl|AgCl–Ag." By D. Feakins and C. M. French.

" Monomethiodides of some 3-substituted 4 : 7-phenanthrolines." By W. O. Sykes.

" The isomeric eudesmols and their association with carissone in *Eucalyptus macarthuri*." By F. J. McQuillin and J. D. Parrack.

" Preparation of 4-substituted 2-dimethylamino-5-nitro- and -5-amino-pyrimidines." By D. G. Saunders.

" The preparation and properties of some plutonium compounds. Part V. Colloidal quadrivalent plutonium." By D. W. Ockenden and G. A. Welch.

" Raman spectra and constitution of solid hydrates. Hydroxonium perchlorate, nitrate, hydrogen sulphate, and sulphate." By D. J. Millen and E. G. Vaal.

" Anhydro-compounds from nitrogen-containing derivatives of thioglycollic acid. Part III. Arylazo-compounds." By G. F. Duffin and J. D. Kendall.

" Polynuclear heterocyclic systems. Part XI. Absorption spectra of compounds containing five-membered rings." By G. M. Badger and B. J. Christie.

" α-1 : 4-Glucosans. Part IV. A re-examination of the molecular structure of Floridean starch." By I. D. Fleming, E. L. Hirst, and D. J. Manners.

" The absorption of uncharged molecules by ion-exchange resins." By D. Reichenberg and W. F. Wall.

" The pyrolysis of chloroalkenes. Part IV. The radical chain decomposition of the 1 : 2-dichloroethylenes." By (Miss) A. M. Goodall and K. E. Howlett.

" Chemistry of the higher fungi. Part VI. Isomerisation reactions of naturally occurring allenes." By J. D. Bu'Lock, E. R. H. Jones, P. R. Leeming, and J. M. Thompson.

" An observation concerning aluminium complexes of flavonols." By J. A. Ballantine and W. B. Whalley.

" Some chlorinated derivatives of phloroglucinol." By G. Lloyd and W. B. Whalley.

" 3-Aroylcoumarones." By W. B. Whalley and (in part) G. Lloyd.

" The degradation of carbohydrates by alkali. Part XII. 6-*O*-Methyl and 3 : 6- and 4 : 6-di-*O*-methyl-D-glucoses." By J. Kenner and G. N. Richards.

" The alkaline degradation of carbohydrates. Part XIII. 2 : 3-Di-*O*-methylglucose and its conversion into 5-hydroxymethylfurfuraldehyde." By J. Kenner and G. N. Richards.

" cyclo*Hexane*-1 : 3-diones. Part I. Hydrolysis of ethyl 2 : 4-dioxo-6-styryl*cyclo*hexanecarboxylate." By G. R. Ames and W. Davey.

" Benzyloxymalondialdehyde. An intermediate in the oxidation of 2-*O*-benzyl-D-arabinose with sodium periodate." By J. C. P. Schwarz and (in part) Myra MacDougall.

" Structure and reactivity of the oxy-anions of transition metals. Part I. The manganese oxy-anions." By A. Carrington and M. C. R. Symons.

" Organic complex-forming agents for metals. Part II. Preparation of 5-hydroxy- and 5 : 8-dihydroxy-quinoxalines and related compounds." By E. S. Lane and C. Williams.

" Buta-1 : 3-diene-2-carboxylic acid." By E. A. Braude and E. A. Evans.

" Alkenylation with lithium alkenyls. Part XIII. 1-Methylvinyl-lithium (*iso*propenyl-lithium)." By E. A. Braude and E. A. Evans.

" Statistical thermodynamic interpretation of the sorption of water and methanol by carbon." By R. M. Barrer and W. I. Stuart.

" Triterpenoids. Part LIII. The constitution and stereochemistry of butyrospermol." By WILLIAM LAWRIE, WILLIAM HAMILTON, F. S. SPRING, and H. S. WATSON.

" Chemical constitution and the dissociation constants of monocarboxylic acids. Part XV. Steric effects in substituted nitrobenzoic acids." By J. F. J. DIPPY, S. R. C. HUGHES, and J. W. LAXTON.

" Absorption spectra of ketones. Part V. γ-Substituted αβ-unsaturated ketones." By C. W. BIRD, R. C. COOKSON, and S. H. DANDEGAONKER.

" The chemistry of the triterpenes and related compounds. Part XXIX. The chemistry of butyrospermol." By M. C. DAWSON, T. G. HALSALL, E. R. H. JONES, G. D. MEAKINS, and P. C. PHILLIPS.

" The chemistry of fluorene. Part V. The preparation of 9 : 9-dialkylfluorenes and the dehydrohalogenation of 9-halogenoalkylfluorenes." By E. J. GREENHOW and D. MCNEIL.

" Purines, pyrimidines, and glyoxalines. Part III. A new synthesis of 2-thiouracils." By M. R. ATKINSON, G. SHAW, K. SCHAFFNER, and R. N. WARRENER.

" The reaction of 3 : 4-dihydro-4-oxobenz-1 : 2 : 3-triazine with phosphorus pentachloride and phosphorus oxychloride." By D. BUCKLEY and M. S. GIBSON.

" Griseoviridin. Part III. Degradation to 10-aminodecanoic acid and other reactions." By D. E. AMES and R. E. BOWMAN.

" Molecular-weight studies of dextran." By G. C. BOOTH and V. GOLD.

" The condensation products of malononitrile and certain cyclic keto-amines." By P. I. ITTYERAH and FREDERICK G. MANN.

" Unsaturated fatty acids. Part II. The synthesis of linolenic acid." By S. S. NIGAM and B. C. L. WEEDON.

" Hydrogen-transfer. Part IX. The selective dehydrogenation of unsaturated alcohols by high-potential quinones." By E. A. BRAUDE, R. P. LINSTEAD, and K. R. WOOLDRIDGE.

" A new synthesis of 6 : 8-thioctic acid." By E. A. BRAUDE, R. P. LINSTEAD, and K. R. H. WOOLDRIDGE.

" The dimerisation of mesityl oxide. A novel type of diene addition." By E. A. BRAUDE, B. F. GOFTON, G. LOWE, and E. S. WAIGHT.

" Quassin and *neo*quassin. Part IV." By R. J. S. BEER, K. R. HANSON, and ALEXANDER ROBERTSON.

" Calciferol and its relatives. Part II. An alternative synthesis of *trans*-1-2′-*cyclo*hexylidene-ethylidene-2-methylene*cyclo*hexane." By B. LYTHGOE, S. TRIPPETT, and J. C. WATKINS.

" The preparation of [2 : 4 : 7 : 9-$^{14}C_1$]phenanthroline and 2 : 2′-[4 : 4′ : 6 : 6′-$^{14}C_1$]dipyridyl." By PETER ELLIS, R. G. WILKINS, and M. J. G. WILLIAMS.

" The interaction of boron trichloride with unsaturated alcohols and ethers." By W. GERRARD, M. F. LAPPERT, and H. B. SILVER.

" Synthesis of cystinol." By J. C. CRAWHALL, D. F. ELLIOTT, and K. C. HOOPER.

" Ferrocene derivatives. Part III. *cyclo*Pentadienyliron carbonyls." By B. F. HALLAM and P. L. PAUSON.

" Thermodynamics of hydrocarbon mixtures. Part II. Heats of mixing of the binary mixtures formed by benzene, *cyclo*hexane, *n*-heptane, toluene, and *n*-hexane." By A. R. MATHIESON and J. C. J. THYNNE.

" Pteridine derivatives. Part III. Bisdihydropurinyls." By W. E. FIDLER and H. C. S. WOOD.

" Notes on four anomalous substitution reactions." By F. BELL.

" Synthesis of tetramethylhydrazine by photolysis and pyrolysis of tetramethyltetrazan." By J. S. WATSON.

" Preparation of 1-oxygenated steroids. The reaction of 3β-hydroxycholest-1-ene with thionyl chloride." By H. B. HENBEST and R. A. L. WILSON.

" The synthesis of (±)-angustione and related compounds." By G. R. ENSOR and W. WILSON.

" *N*-Oxides of some hydroxy- and amino-quinolines." By D. E. AMES, C. S. FRANKLIN, and T. F. GREY.

"The preparation *via* thiuronium salts, of optically active thiols." By C. L. ARCUS and P. A. HALLGARTEN.

"Researches on acetylenic compounds. Part LII. The preparation and anomalous absorption spectra of some *bicyclo*[2 : 2 : 1]heptane derivatives." By E. R. H. JONES, G. H. MANSFIELD, and M. C. WHITING.

"Some new analogues of pethidine. Part I." By R. J. ANDERSON, P. M. FREARSON, and E. S. STERN.

"Colouring matters of the aphididae. Part XV. The alkaline inversion of erythro-aphin-*sl* and its derivatives." By A. W. JOHNSON, SIR ALEXANDER TODD, and J. C. WATKINS.

"Hydropteridines. Part IV. 5 : 6 : 7 : 8-Tetrahydropteridine." By P. R. BROOK and G. R. RAMAGE.

"Lactones. Part III. A further example of alkyl–oxygen bond fission in phthalide ring opening." By JOHN BLAIR, W. R. LOGAN, and G. T. NEWBOLD.

"The viscosities of iodine pentafluoride and ditellurium decafluoride." By G. HETHERINGTON and P. L. ROBINSON.

"*Aconitum* and *delphinium* alkaloids. Part II. Inter-relation of the functional groups of delpheline." By R. C. COOKSON and M. E. TREVETT.

"The constituents of *Casimiroa edulis* Llave *et* Lex. Part I. The seed." By F. A. KINCL, J. ROMO, G. ROSENKRANZ, and FRANZ SONDHEIMER.

"The constituents of *Casimiroa edulis* Llave *et* Lex. Part II. The bark." By J. IRIARTE, F. A. KINCL, G. ROSENKRANZ, and FRANZ SONDHEIMER.

"4-Hydroxy*iso*phthalic acid." By S. E. HUNT, J. IDRIS JONES, and A. S. LINDSEY.

"Elaboration products of eucarvone." By J. R. B. CAMPBELL, A. M. ISLAM, and R. A. RAPHAEL.

"The hydrolysis of 3 : 5-dinitrobenzoates." By J. CASTELLS and G. A. FLETCHER.

"A search for new trypanocides. Part II. 4-Amino-6-dialkylaminoquinaldines." By H. BADER.

"Tetronic acids and related compounds. Part I. Synthesis from α-hydroxy-esters." By L. J. HAYNES and A. H. STANNERS.

"Some observations on the sulphonation of diphenyl sulphide." By J. CHATT and A. A. WILLIAMS.

"The oxidation of derivatives of *o*-phenylenediamine. Part IV. A new series of glyoxalinophenazines derived from anilino*apo*safranines and their behaviour on hydrogenation." By VINCENT C. BARRY, J. G. BELTON, J. F. O'SULLIVAN, and DERMOT TWOMEY.

"A new synthesis of 4-hydroxycoumarins." By J. F. GARDEN, N. F. HAYES, and R. H. THOMSON.

"2-Acyl derivatives of cyclic 1 : 3-diones. Part III. Ultraviolet and infrared absorption spectra of 2-acyl*cyclo*hexane-1 : 3-diones." By W. R. CHAN and C. H. HASSALL.

"Studies on the Diels–Alder reaction. Part IV. Reduction products of *cis-syn*-1 : 4 : 5 : 6 : 12 : 13 : 14 : 15-octahydro-8-methoxy-1 : 4-dioxochrysene and their interrelation." By P. A. ROBINS and JAMES WALKER.

"A new and specific aromatisation reaction. Part I." By P. A. ROBINS and JAMES WALKER.

"The heat of hydrolysis of ethyl orthosilicate and of chlorotriethoxysilane." By T. FLITCROFT and H. A. SKINNER.

ADDITIONS TO THE LIBRARY

Acridines, by R. M. Acheson, with a chapter by L. E. Orgel. (The Chemistry of Heterocyclic compounds, a series of monographs, edited by A. Weissberger. Vol. 9. Interscience Publishers, Inc. 1956.

Physics and chemistry of the earth, edited by L. H. Ahrens, Kalervo Rankama and S. K. Runcorn. Vol. 1. Pergamon Press. 1956. (Presented by the Publishers.)

Determination of toxic substances in the air of industrial premises, by M. V. Alekseyeva, B. Ye. Andronov, S. S. Gurvits, and A. S. Zhitkova. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

The properties and microstructure of uranium dioxide; their dependence upon the mode of preparation, by J. S. Anderson, E. A. Harper, S. Moorbath, and L. E. J. Roberts. (Atomic Energy Research Establishment C/R 886.) Atomic Energy Research Establishment. 1955.

The applications of latex to textile and allied materials, by C. M. Blow. (Natural Rubber Latex and its Applications, No. 5.) Natural Rubber Development Board. 1956. (Presented by the Publishers.)

The determination of rubidium and cæsium in sodium–potassium alloys and related materials by radioactivation, by M. J. Cabell and A. Thomas. (Atomic Energy Research Establishment C/R 1725.) Atomic Energy Research Establishment. 1955.

Production of azo-dyes, by M. A. Chekalin and F. F. Yeremin. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Untersuchungen über Aceton als Lösungsmittel für Acetylen. Forschungsstelle für Acetylen, Dortmund. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 14.) Westdeutscher Verlag. 1952. (Presented by the Publisher.)

Über die Zustandsgleichung des gasförmigen Acetylens und das gleichgewicht Acetylen-aceton. Forschungsstelle für Acetylen, Dortmund. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 78.) Westdeutscher Verlag. 1954. (Presented by the Publisher.)

Molecular volume and structure, by T. W. Gibling. In manuscript. (Presented by the Author.)

Gmelins Handbuch der anorganischen Chemie. Calcium, Teil B—Lieferung 1, Technologie. System-nummer 28. 8th edn. Verlag Chemie, GMBH. 1956.

Alloys of iron with chromium and manganese, by A. T. Grigor'ev. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Einführung in die Chemie der komplexverbindungen, by A. A. Grinberg. Veb Verlag Technik. 1955.

Untersuchungen über den Druckverlauf bei der explosiblen Zersetzung von gasförmigem Acetylen, by Hölemann, P. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 110.) Westdeutscher Verlag. 1954. (Presented by the Publisher.)

Untersuchungen über die Löslichkeit von Azetylen in verschiedenen organischen Lösungsmitteln, by P. Hölemann and R. Hasselmann. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 109.) Westdeutscher Verlag. 1954. (Presented by the Publisher.)

Untersuchungen über die thermische Zündung von explosiblen Acetylenzersetzungen in Kapillaren, by P. Hölemann, R. Hasselmann and G. Dix. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 102.) Westdeutscher Verlag. 1954. (Presented by the Publisher.)

Applied mass spectrometry. Report of a conference organized by the Mass Spectrometry Panel of the Institute of Petroleum, and held in London, 1953. Institute of Petroleum. 1954.

Luminescence (with particular reference to solid inorganic phosphors). A symposium held by the Electronics Group of the Institute of Physics at Cambridge, 1954. British Journal of Applied Physics, 1955, Supplement No. 4. Institute of Physics. 1955.

Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, held in Geneva, 1955. Vol. 7, Nuclear chemistry and effects of irradiation. Vol. 9, Reactor technology and chemical processing. Vol. 15, Applications of radioactive isotopes and fission products in research and industry. United Nations. 1956.

Organomagnesium compounds, by S. T. Ioffe and A. N. Nesmeyanov. 3 vols. (In Russian.) 1950. (Presented by the U.S.S.R. Academy of Sciences.)

Eine Methode zur Bestimmung von Schwefeldioxyd und Schwefelwasserstoff in Rauchgasen und in der Atmosphäre. Kohlenstoffbiologische Forschungsstation e. V. (Forschungsberichte des Wirtschafts- und Verk-

kehrsministeriums Nordrhein-Westfalen, edited by L. Brandt. Nr. 33.) Westdeutscher Verlag. 1953. (Presented by the Publisher.)

Phase equilibria in solution at high pressures, by I. R. Krichevskii. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Advances in biological and medical physics, edited by J. H. Lawrence and C. A. Tobias. Vol. 4. Academic Press Inc. 1956.

Industrial poisons. Part 1, Organic substances. Part 2, Inorganic and elementary organic compounds. Edited by N. V. Lazarev. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

Chemistry of herbicides and plant-growth promoters, by N. N. Mel'nikov, Yu. A. Baskakov, and K. S. Bokarev. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

D.D.T.: properties and use, by N. N. Mel'nikov, V. A. Nabokov, and Ye. A. Pokrovskii. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

Lithium aluminum hydride in organic chemistry, by Vukić M. Mićovic and Mihailo Lj. Mihailović, edited by Kosta V. Petković. (Serbian Academy of Sciences, Monographs, Vol. 237. Section for Natural Sciences and Mathematics, No. 9.) Serbian Academy of Sciences. 1955.

Alloys of magnesium with aluminium and zinc, by V. I. Mikheyeva. (In Russian.) 1946. (Presented by the U.S.S.R. Academy of Sciences.)

Chemical nature of very strong alloys of aluminium with magnesium and zinc, by V. I. Mikheyeva. (In Russian.) 1947. (Presented by the U.S.S.R. Academy of Sciences.)

Handbook on solubility of salt systems. Vol. I. By Ministerstvo Khimicheskoi Promyshdennosti S.S.S.R. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Chemistry of steroid hormones, by I. N. Nazarov and L. D. Bergel'son. (In Russian.) 1955. (Presented by the U.S.S.R. Academy of Sciences.)

Chemistry of alkaloids, by A. P. Orekhov. (In Russian.) 1955. (Presented by the U.S.S.R. Academy of Sciences.)

De reactie van phenol met formaldehyde. Onderzoekingen met behulp van papierchromatografie, by H. G. Peer. Uitgeverij Excelsior. 1956. (Presented by the Publishers.)

Biographisch-literarisches handwörterbuch der exakten naturwissenschaften. Band VIIa. Teil 1: A—E. 2. Lieferung. By J. C. Poggendorf. Akademie-Verlag. 1956.

Chemistry of organic medicinals, by N. A. Preobrazhenskii and E. I. Genlein. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Phase structure of triglycerides, by G. V. Ravich and G. G. Tsurinov. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Chemistry of antibiotics, by M. M. Shemyakin and A. S. Khokhlov. (In Russian.) 1953. (Presented by the U.S.S.R. Academy of Sciences.)

Synthetic rubbers, by N. I. Smirnov. 2nd edn. (In Russian.) 1954. (Presented by the U.S.S.R. Academy of Sciences.)

Methods of handling radioactive indicators, by V. I. Spitsyn, P. N. Kodochigov, M. M. Golutvina, A. F. Kuzina, and Z. A. Sokolova. (In Russian.) 1955. (Presented by the U.S.S.R. Academy of Sciences.)

Reacties van Aminozuren en Peptiden met Aromatische Aldehyden, by E. L. T. M. Spitzer. Uitgeverij Excelsior. 1956. (Presented by the Publishers.)

Die Physik der Hochpolymeren, edited H. A. Stuart. Vol. 4. Theorie und molekulare Deutung technologischer Eigensschaften von Hochpolymeren Werkstoffen, edited by J. P. Berry *et al.* Springer-Verlag. 1956.

Photochemistry of dyes, by A. N. Terenin. (In Russian.) 1947. (Presented by the U.S.S.R. Academy of Sciences.)

Chromatographic adsorption analysis. Selected papers by M. S. Tswett, edited by A. A. Richter and T. A. Krasnosselskaja. (In Russian.) 1946. (Presented by the U.S.S.R. Academy of Sciences.)

De alkalische hydrolyse van de aethylesters van enige α-aminozuren, by J. Van De Poel. Uitgeverij Excelsior. 1956. (Presented by the Publishers.)

General chemical technology, by S. I. Vol'fkovich, A. P. Yegorov and D. A. Epshtein. Vol. I. (In Russian.) 1952. (Presented by the U.S.S.R. Academy of Sciences.)

Technique of organic chemistry, edited by A. Weissberger. Vol. 9. Chemical applications of spectroscopy, by A. B. F. Duncan, Walter Gordy, E. Norman Jones, F. A. Matsen, Camille Sandorfy and W. West, edited by W. West. Interscience Publishers, Inc. 1956.

The preparation of plutonium amalgam and its reaction with dilute hydrochloric acid, by A. G. White. (Atomic Energy Research Establishment C/R 1468.) Atomic Energy Research Establishment. 1955.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, B.Sc., M.A., Ph.D., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
,,	G. D. Meakins, M.A., D.Phil., Chemistry Department, The University, Manchester, 13.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
,,	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham and Leicester	T. J. King, B.Sc., M.A., D.Phil., Chemistry Department, The University, University Park, Nottingham.
,,	E. R. A. Peeling, B.Sc., Ph.D., University College, Leicester.
Oxford.	R. E. Richards, M.A., D.Phil., Lincoln College, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	N. B. Chapman, M.A., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.
,,	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
John Broadhouse Herbert Beards (Birmingham)	Dec. 4th, 1919.	Aug. 1955.
Gustav Jim Östling (Helsinki)	June 19th, 1924.	Apr. 29th, 1955.
Martha Annie Whiteley (London) (C. 1928/31) ...	Dec. 2nd, 1920.	May 24th, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows whose names appeared in the Birthday Honours List for 1956:

C.B.E.
Frank Philip Bowden (Cambridge).
Foster Neville Woodward (Gullane).

ELECTION OF NEW FELLOWS.

Honorary Fellows

The following were elected Honorary Fellows of the Society on June 7th, 1956:

Robert Sanderson Mulliken (Chicago).
Robert Burns Woodward (Harvard).

Fellows

The following 29 candidates were elected Fellows of the Society on June 7th, 1956:

Manuel Aroney.
Bal Krishna Avasthi.
Jehanbux Framroz Bagli.
Lionel Cyril Francis Blackman.
John Warren Blaker.
John Arthur Broomhead.
Reginald William Kell Cook.
John Michael Crawford.
Richard James William Campbell-Davys Cremlyn.
Morris Dunkel.
Ronald Hilson Begg Galt.
Ian Hampson Gibson.
Patrick Gould.
George Solomon Hartman.
Margarita Karelsky.
Ronald Walter Lincolne Kimber.
Nicholas Kowanko.
Reuben Sydney Leach.
Zbigniew Jan Okolski.
David Charles Priest.
Douglas William Russell.
Sidney Frank Simon.
Lynne Sinclair.
Sambasiva Swaminathan.
Nigel Hardy Taylor.
Philip Bernard Hague Tinker.
Edwin F. Ullman.
Alan George Walton.
Alan John Williams.

ACKNOWLEDGMENTS.

The thanks of the Society have been conveyed to the executors of the late Dr. A. F. Campbell, who bequeathed his set of the Annual Reports to the Society, and to the National Oil Refineries, Ltd. (B.P.), Llandarcy, for a gift of publications of the Society.

LOCAL REPRESENTATIVES.

The following appointments have been made :

Manchester : Dr. G. D. Meakins in place of Dr. H. B. Henbest.

Nottingham and Leicester : Dr. T. J. King in place of Dr. C. C. Addison. Dr. E. R. A. Peeling (Leicester) to act jointly with the Local Representative for Nottingham.

Oxford : Dr. R. E. Richards in place of Mr. L. A. K. Staveley.

The President has conveyed the thanks of the Society to the retiring Local Representatives for their services to the Society.

THE HARRISON MEMORIAL PRIZE

In accordance with the Trust Deed governing the Harrison Memorial Fund, the Selection Committee, consisting of the Presidents of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the Pharmaceutical Society, will, after December 1st, 1956, consider making an award of the Harrison Memorial Prize.

The Prize, not exceeding 100 Guineas, will be awarded to the chemist of either sex, being a natural-born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, shall, during the previous five years, have conducted the most meritorious and promising original investigations in chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should give the name of the applicant (in full), age (birth certificate should accompany the application), degrees (with name of University), any other qualifications and experience, titles of published papers (with co-authors' names) including full references to publication, where research was carried out, testimonials and references, and any other particulars bearing on the application.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates eligible for the Prize. Any such communication must be received by the President, The Chemical Society, Burlington House, Piccadilly, London, W.1, not later than Saturday, December 1st, 1956. Candidates must not have attained the age of thirty years at this date.

CORDAY-MORGAN MEDAL AND PRIZE.

This Award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 are due before the end of 1957.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in November next. All persons who have received grants, and whose accounts have not been declared closed by the Council, are informed that reports must be received by the Society not later than November 1st, 1956.

Applications for grants, to be made on forms available from the General Secretary, must be received on or before November 15th, 1956. Applications from Fellows will receive prior consideration.

Attention is drawn to the fact that the income arising from the donation of the Worshipful Company of Goldsmiths is principally devoted to the encouragement of research in

inorganic and metallurgical chemistry and that the income from the Perkin Memorial Fund is to be applied to investigations relating to problems connected with the coal-tar and allied industries.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at Burlington House on Thursday June 7th, 1956, at 7.30 p.m.

The President, Professor E. L. Hirst, M.A., D.Sc., F.R.S., was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at Burlington House on Thursday, May 3rd, 1956, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: George S. Hammond, J. C. Williams, B. M. Luckett, W. S. Crisp, S. Neelakantan, B. C. Easton, P. J. Richardson, E. J. Sparrow, John Milsted, K. F. Watterson, Peter J. Haines, H. G. Baxter, D. J. B. Potter, R. J. Otter, J. W. Ducker, Elizabeth Rhodes, G. M. Saul, G. S. Ingram, R. A. Jones, P. M. Woodhams, S. W. Bell, Geoffrey Wilkinson, E. D. Nickels, J. C. Lockhart, D. L. Hill, Lidia Vallarino, B. M. Gatehouse.

CENTENARY LECTURE.

The President called upon Professor G. T. Seaborg to deliver the Centenary Lecture entitled "The Present Status of the Transuranium Elements." At the conclusion of the Lecture, a vote of thanks to Professor Seaborg, proposed by Professor H. J. Emeléus, was carried with acclamation.

LIST OF APPLICATIONS FOR FELLOWSHIP

(*Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of the publication of the* Journal *for July*, 1956. *Such objections will be treated as confidential. The forms of application are available in the Library.*)

Bull, John, B.Sc. (Lond.). British. 9, Lilburne Road, Eltham, S.E.9. Experimental Officer with the U.K. Atomic Energy Authority. *Signed by:* C. M. Bere, A. W. Westrup.

Capel, Thomas Ronald. British. 7, St. Mary's Avenue, Finchley, N.3. Technical Assistant to Chartered Patent Agents. *Signed by:* E. W. Moss, L. A. Haddock.

Coe, Colin Gerald. British. 81, Mill Road, Kettering, Northants. National Service. *Signed by:* G. Read, J. W. Gramshaw.

Feilchenfeld, Hans, M.Sc. and Ph.D. (Jerusalem). Israeli. 33, King George Avenue, Jerusalem, Israel. Research Director. *Signed by:* M. Neeman, G. Stein.

Hambling, James Keith, B.Sc. (Manc.). British. 7, Cornwall Gardens, London, S.W.7. Research Student at King's College. *Signed by:* S. H. Harper, D. H. Hey.

Hamor, Thomas Andrew, B.Sc. (Glas.). British. 17, Spence Street, Glasgow, N.W. Research Chemist. *Signed by:* D. S. Payne, J. Bell.

Ittyerah, Puthupparambil Ittyerah, B.A. (Madras), M.Sc. and Ph.D. (Agra), A.R.I.C. Indian. Department of Chemistry, St. John's College, Agra, India. Head of Chemistry Department, St. John's College. *Signed by:* R. N. Haszeldine, F. G. Mann.

Jones, John Bryan, B.Sc. (Wales). British. Chemistry Department, University College, Cardiff. Research Student. *Signed by:* A. R. Pinder, A. G. Evans.

Krentos, Vlassios, B.Sc. (Manc.), A.R.I.C. British. 10, Warren Road, Filton, Bristol. Agricultural Chemist. *Signed by:* J. R. Quayle, R. Long.

Lorenz, Carl Edward, B.A. (New York). American. 85–38, 52 Avenue, Elmhurst 73, New York, U.S.A. Teaching Fellow. *Signed by:* B. Arnowich, R. N. Boyd.

Mandleberg, Charles John, B.Sc. and M.A. (Oxon.) A.R.I.C. British. Farringdon House, St. Helen's Road, Leigh, Lancs. Research Chemist with Messrs. Harbens, Ltd., Warrington. *Signed by:* H. Irving, J. H. Mandleberg.

Meister, Alton, B.S. (Harvard), M.D. (Cornell). American. Department of Biochemistry, Tufts Medical School, 136, Harrison Avenue, Boston, Massachusetts, U.S.A. Professor of Biochemistry. *Signed by:* A. A. Patchett, H. G. Fletcher.

Perkins, Norman Albert. British. 47, Sedlescombe Road, Fulham, S.W.6. Research Laboratory Assistant. *Signed by:* J. F. J. Dippy, A. M. James.

Petersen, George Bouet, M.Sc. (New Zealand). British. c/o Department of Biochemistry, South Parks Road, Oxford. Student. *Signed by:* M. V. Kelemen, R. B. Clayton.

Pockley, Robert Peter Campbell. Australian. 15, Chester Street, Geelong, Victoria, Australia. Student. *Signed by:* K. H. Pausacker, B. M. Lynch.

Solomons, Cyril, B.Sc. and Ph.D. (Lond.). British. 28, Margetson House, Stamford Hill, N.16. Lecturer. *Signed by:* E. D. Hughes, R. J. Gillespie.

Sutcliffe, Leslie Howard, B.Sc. (Lond.), Ph.D. (Leeds). British. Department of Inorganic and Physical Chemistry, The University, Liverpool. Lecturer. *Signed by:* A. K. Holliday, G. Skirrow.

Swindells, Margaret Louise, B.A. and B.Sc. (Oxon.). British. 33, Phipson Road, Sparkhill, Birmingham 11. Research Chemist at Shell Research Ltd. *Signed by:* M. L. Tomlinson, L. J. Goldsworthy.

Thomas, William John, B.Sc. (Wales), Ph.D. (Lond.), D.I.C. British. Department of Chemistry, University College, Swansea. Assistant Lecturer. *Signed by:* K. W. Sykes, C. W. Shoppee.

Waters, Brian Thomas, B.Sc. (Bris.). British. Department of Chemistry, University of Bristol, Woodland Road, Bristol 8. Research Student. *Signed by:* F. S. Stone, P. Woodward.

Weinheimer, Alfred John, M.S. (Canisius College), Ph.D. (Duke). American. Department of Chemistry, Wayne University, Detroit 1, Michigan, U.S.A. Post-Doctoral Fellow. *Signed by:* G. H. Alt, C. Djerassi.

Willner, David, M.Sc. (Jerusalem). Israeli. 12, Hayarden Street, Tel-Aviv, Israel. Research Assistant at Weizmann Institute of Science. *Signed by:* M. Neeman, D. Elad.

Wilmot, Philip Daryl, B.Sc. (Q.U.B.). British. Rosaire, Highfield Drive, Uxbridge, Middlesex. Development Chemist with the Mond Nickel Co. *Signed by:* J. W. Barrett, D. V. N. Hardy.

Yates, John Allan, B.Sc. (Dunelm). British. 66, Manchester Road, Prescot, Lancs. Research Chemist with Pilkington Brothers, Ltd. *Signed by:* M. N. Leathwood, W. B. Price.

Zissell, Martin John. British. 110, Cat Hill, East Barnet, Herts. Student at St. John's College, Oxford. *Signed by:* L. A. K. Staveley, T. G. Halsall.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Berman, Herbert I., A.B. (Pennsylvania), M.S. (Purdue). American. 409, Harrison Street, West Lafayette, Indiana, U.S.A. Student at Purdue University. *Signed by:* P. Smith.

Di Fonzo, Maria, D.Pharm. (Bari), D.Chem. (Bologna). Italian. Istituto di Chimica Farmaceutica, Universita di Bari, Italy. Teaching Pharmaceutical Chemistry. *Signed by:* R. de Fazi.

Moriondo, Antonio, D.Chem. (Turin). Italian. Corso Vittorio Emanuele 44, Torino, Italy. Director of Sales Department, Schiapparelli S.p.A., Torino. *Signed by:* U. Croatto.

Tooley, David Frank. British. 6 Petroleum Laboratory, R.A.S.C., c/o 4 SRD, R.A.S.C., c/o G.P.O., Singapore. N.C.O. i/c Laboratory. *Signed by:* D. A. Conyers.

Tsou, K. C., Ph.D. (Nebraska). Chinese. 63, Belmont Road, Leominster, Massachusetts, U.S.A. Research Chemist. *Signed by:* Ching Yuan.

PAPERS ACCEPTED

(List of Papers accepted between May 18th and June 21st, 1956, for publication in the *Journal.*)

"Studies on phosphorylation. Part XIV. The solvolysis by phenols of benzyl phosphates." By G. W. KENNER and J. MATHER.

"A conductivity method for the accurate determination of carbon in low-carbon steels." By D. F. DAILLY and T. A. ELLIOTT.

"Ethyl *p*-nitrobenzoylethoxaloacetate." By J. FORREST, S. B. HANSEN, and V. PETROW.

"Co-ordination compounds between ethylenediaminetetra-acetic acid and gallium, indium, and thallium." By KAZUO SAITO and (the late) HENRY TERREY.

"The thermal decomposition of oxamide." By F. M. TAYLER and L. L. BIRCUMSHAW.

"The fate of methyl radicals in the mechanism of thermal decomposition of metal alkyls." By L. H. LONG.

"The chemistry of fungi. Part XXVI. Dechloronornidulin." By F. M. DEAN, A. D. T. ERNI, and ALEXANDER ROBERTSON.

" The reactivity of 2-bromopent-2-enoic acid." By B. J. P. Alles and M. U. S. Sultanbawa.

" Possible *f*-orbital hybridization in uranyl and related complexes." By C. A. Coulson and G. R. Lester.

" The structure of N_β-alkyl-β-carboline anhydro-bases." By Ian D. Spenser.

" Pteridine studies. IX. The structure of the monohydroxypteridines and their *N*-methyl derivatives." By D. J. Brown and S. F. Mason.

" The decomposition of mercury fulminate." By B. E. Bartlett, F. C. Tompkins, and D. A. Young.

" The decomposition of lead styphnate monohydrate." By F. C. Tompkins and D. A. Young.

" The polarography of oximes." By H. J. Gardner and W. P. Georgans.

" Studies in pyrolysis. Part VII. Model systems for the pyrolysis of poly(ethylene terephthalate); 2 : 2′-dibenzoyloxydiethyl ether, 2-benzoyloxyethyl vinyl ether, and certain related vinyl ethers." By H. V. R. Iengar and P. D. Ritchie.

" Electrophilic substitution. Part III. The nitration of phenanthrene." By M. J. S. Dewar and E. W. T. Warford.

" Electrophilic substitution. Part IV. The nitration of diphenyl, chrysene, benzo[*a*]pyrene, and anthanthrene." By M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford.

" Electrophilic substitution. Part V. Competitive nitrations." By M. J. S. Dewar, T. Mole, and E. W. T. Warford.

" Electrophilic substitution. Part VI. The nitration of aromatic hydrocarbons: partial rate factors and their interpretation." By M. J. S. Dewar, T. Mole, and E. W. T. Warford.

" The crystal and molecular structure of pteridine." By T. A. Hamor and J. Monteath Robertson.

" Perfluoroalkyl derivatives of nitrogen. Part IV. The synthesis, properties, and infrared spectra of perfluoroalkyl *iso*cyanates and carbamates." By D. A. Barr and R. N. Haszeldine.

" Magnetic studies with copper(II) salts. Part I. Anomalous paramagnetism and bonding in anhydrous and hydrated copper(II) acetates." By B. N. Figgis and R. L. Martin.

" The fluorination of tellurium. Ditellurium decafluoride and tellurium oxyfluorides." By R. Campbell and P. L. Robinson.

" The polonium halides. Part III. Polonium tetraiodide." By K. W. Bagnall, R. W. M. D'Eye, and J. H. Freeman.

" Synthesis of lapachenole." By R. Livingstone and R. B. Watson.

" The kinetics of alkyl–oxygen fission in ester hydrolysis. Part V. Olefin formation." By J. C. Hawke and V. R. Stimson.

" Nucleotides. Part XXXVIII. An improved synthesis of uridine-diphosphate-glucose (UDPG)." By A. M. Michelson and Sir Alexander Todd.

" Anomalies in the reduction of 2 : 2′-diacetyldiphenyl." By D. Muriel Hall, Joan E. Ladbury, Mary S. Lesslie, and E. E. Turner.

" Dielectric properties of some aluminium soaps and their solutions in toluene." By S. M. Nelson, A. Gilmour, and R. C. Pink.

" Cytidine nucleotides. Part III. A cytidine-diphosphate-glycerol." By J. Baddiley, J. G. Buchanan, A. P. Mathias, and A. R. Sanderson.

" *peri*-Hydroxycarbonyl compounds. Part II. The effect of ring size on hydrogen bonding." By V. C. Farmer, N. F. Hayes, and R. H. Thomson.

" Heterocyclic imines and amines. Part VII. *N*-Substituted phthalic imidine derivatives and their reactions with amines." By P. F. Clark, J. A. Elvidge, and J. H. Golden.

" Compounds containing directly linked pyrrole rings. Part II. Dialkylamino-β-*iso*indigos." By J. A. Elvidge and J. H. Golden.

"Calculated bond lengths in some cyclic compounds. Part IV. Pteridine and melamine, and a correlation curve for C–N bonds." By T. H. GOODWIN and A. L. PORTE.

"The preparation of the half esters of phthalic acid and of 3-nitrophthalic acid." By M. K. HARGREAVES.

"The distribution of ester groups in dextran sulphate and their stability toward hydrolytic reagents." By C. R. RICKETTS.

"Chemical action of ionising radiations in solutions. Part XVI. Formation of labile phosphate esters from purine and pyrimidine ribonucleotides by irradiation with *X*-rays in aqueous solution." By M. DANIELS, G. SCHOLES, and J. WEISS.

"Diaryl-2 : 2′-disulphonic acids and related compounds. Part II. The optical stability of a cyclic 2 : 2′-thiosulphonate." By W. L. F. ARMAREGO and E. E. TURNER.

"The structure of the extracellular polysaccharide of *Aerobacter aerogenes* A3 (S1) (Klebsiella type 54)." By G. O. ASPINALL, R. S. P. JAMIESON, and J. F. WILKINSON.

"The preparation of active solids by thermal decomposition. Part IX. The calcination of hydrous ferric oxide and of lepidocrocite." By J. F. GOODMAN and S. J. GREGG.

"Structural chemistry of the alkoxides. Part VII. Secondary alkoxides of quadrivalent cerium and thorium." By D. C. BRADLEY, A. K. CHATTERJEE, and W. WARDLAW.

"The synthesis of indeno[2,1-*a*]perinaphthene." By I. M. AITKEN and D. H. REID.

"The alleged occurrence of vitamin A in baker's yeast." By F. W. HEATON, J. S. LOWE, and R. A. MORTON.

"Physical properties and chemical constitution. Part XXV. (*a*) Determination of the orientation polarization of alkylpyridines in benzene solutions by two independent methods. (*b*) Dipole moments of alkylpyridines." By C. W. N. CUMPER, A. I. VOGEL, and S. WALKER.

"Synthesis of heterocyclic compounds from ß-unsaturated 1 : 3-diketo-esters." By GABRA SOLIMAN and LATIF RATEB.

"The kinetics of alkyl–oxygen fission in ester hydrolysis. Part VI. Diphenylmethyl esters in aqueous acetone." By G. J. HARVEY and V. R. STIMSON.

"Infrared spectra and polar effects. Part V. Steric restrictions of polar effects and their application in studies on rotational isomerism." By L. J. BELLAMY, L. C. THOMAS, and R. L. WILLIAMS.

"Interaction of Lewis acids with aromatic hydrocarbons and bases. Part XVII. The association of hexamethylbenzene with substituted *p*-benzoquinones in carbon tetrachloride solution." By R. FOSTER, D. LL. HAMMICK, and P. J. PLACITO.

"The kinetics and mechanisms of addition to olefinic substances. Part III. The carbonium ionic intermediate involved in addition of hypochlorous acid to *iso*butene." By P. B. D. DE LA MARE and ADIB SALAMA.

"The electrical conductance of solutions in nitric acid. Part I. Solutions of dinitrogen pentoxide, and of water. The extent of the self-dissociation of nitric acid." By W. H. LEE and D. J. MILLEN.

"The preparation of 4-amino- and other pteridines." By R. M. EVANS, P. G. JONES, P. J. PALMER, and F. F. STEPHENS.

"Potential thiophen chemotherapeutics. Part V. Preparation and proof of structure of some substituted 5-aminothiophen-2-sulphonamides." By J. CYMERMAN-CRAIG, G. N. VAUGHAN, and W. K. WARBURTON.

"Co-ordination complexes of methyl derivatives of indium and thallium." By G. E. COATES and R. A. WHITCOMBE.

"Radical exchange in organometallic compounds. Part I. The replacement of methyl by trifluoromethyl." By R. N. HASZELDINE and B. O. WEST.

"The mesomorphic behaviour of the fatty esters of cholesterol." By G. W. GRAY.

"The reaction of oximes with *iso*propyl methylphosphonofluoridate (Sarin)." By A. L. GREEN and B. SAVILLE.

"Studies of the amino-*iso*quinolines, -cinnolines, and -quinazolines. (*A*) The basic strengths and ultraviolet absorption spectra." By A. R. OSBORN and K. SCHOFIELD. "(*B*) The infrared spectra." By L. N. SHORT.

"Cinnolines. Part XXXV. Studies of the chloro- and hydroxy-cinnolines." By A. R. OSBORN and K. SCHOFIELD.

" The 3-methylcholestanols and their derivatives." By D. H. R. BARTON, A. DA S. CAMPOS-NEVES, and R. C. COOKSON.

" The mechanisms of inhibition and retardation in radical polymerizations. Part III. The use of a stable free radical as an inhibitor." By J. C. BEVINGTON and N. A. GHANEM.

" Transport to the surface of a rotating disc." By D. P. GREGORY and A. C. RIDDIFORD.

" Bitter principles of the Cucurbitaceae. Part IV. Dehydrogenation of cucurbitacin A." By P. R. ENSLIN and D. E. A. RIVETT.

" Sulphanilamide derivatives : compounds derived from 2- and 4-aminoquinazoline and 1-aminophthalazine." By H. J. RODDA.

" Purines, pyrimidines, and glyoxalines. Part IV. Cyanouracils from amines and amino-acids." By M. R. ATKINSON, G. SHAW, and R. N. WARRENER.

" The aporphine series. Part II. Application of the Bischler–Napieralski reaction to 2-nitrophenyl-*N*-phenethylacetamides." By D. H. HEY and A. L. PALLUEL.

" Thermodynamics of hydrocarbon mixtures. Part III. The heats of mixing of ternary, quaternary, and quinary mixtures formed by benzene, *cyclo*hexane, *n*-heptane, toluene, and *n*-hexane." By A. R. MATHIESON and J. C. J. THYNNE.

" Fluorine-substituted polycyclic compounds." By G. M. BADGER and J. F. STEPHENS.

" The lupin alkaloids. Part XVI. The synthesis of externally compensated lupanine." By G. R. CLEMO, R. RAPER, and J. C. SEATON.

" Further substitution in 5-substituted benziminazoles." By R. D. BROWN and M. L. HEFFERNAN.

" Retardation of the chain-decomposition of benzoyl peroxide by polycyclic aromatic hydrocarbons." By J. J. BATTEN.

" The formation of *iso*but-1-enyl radicals from *iso*but-1-enylsilver. Part II." By F. GLOCKLING.

" The preparation of uniformly ^{14}C-labelled substances on a laboratory scale, with special reference to L-tryptophan." By C. E. DALGLIESH and R. W. DUTTON.

" An apparatus for preparative photosynthesis of ^{14}C-labelled substances." By R. W. DUTTON and C. E. DALGLIESH.

" The rates of reaction of copper, zinc, and uranium with organic solvent–dinitrogen tetroxide mixtures." By C. C. ADDISON, J. C. SHELDON, and (in part) N. HODGE.

" A search for new trypanocides. Part III. Some analogues of Suramin." By A. ADAMS, J. N. ASHLEY and H. BADER.

" Some derivatives of 4-propylpyridine and 5 : 6-benzoquinoline." By C. W. REES.

" Studies in peroxidase action. Part XI. The oxidation of a mixture of amines." By G. M. K. HUGHES and B. C. SAUNDERS.

" The structure of pulcherrimin." By A. H. COOK and C. A. SLATER.

" Pulcherrimin—a synthesis of 1 : 4-dihydroxy-2 : 5-dioxopiperazines." By A. H. COOK and C. A. SLATER.

" Studies in relation to biosynthesis. Part VIII. The structure of mycelianamide." By A. J. BIRCH, R. A. MASSY-WESTROPP, and R. W. RICKARDS.

" The Janovsky reaction." By M. J. NEWLANDS and F. WILD.

" Polypeptides. Part IV. The self-condensation of the esters of some peptides of glycine and proline." By H. N. RYDON and P. W. G. SMITH.

" The resolution of secondary and tertiary alcohols containing the pyridyl group." By ALWYN G. DAVIES, J. KENYON, and KUMAR THAKER.

" Modification of the procedure for converting nitriles into aldehydes." By (MRS.) T. STEPHEN and HENRY STEPHEN.

" The preparation of methyl and ethyl β-amino-α-(*N*-substituted benzimidoyl)crotonates and their conversion into methyl and ethyl 3-methyl-1 : 5-diphenylpyrazole-4-carboxylates." By B. STASKUN and H. STEPHEN.

" The racemisation of 9 : 10-dihydro-3 : 4-5 : 6-dibenzophenanthrene." By D. MURIEL HALL.

" A note on the effect of solvent on the rates of solvolysis of 1 : 2-dichloro-2-methylpropane and of 3-chloro-2-methylprop-1-ene, and the rearrangement of the latter chloride in formic acid." By P. B. D. DE LA MARE, K. LEFFEK, and ADIB SALAMA.

ADDITIONS TO THE LIBRARY

Mass spectrometer researches, by G. P. Barnard. (National Physical Laboratory.) H.M.S.O. 1956. (Presented by the National Physical Laboratory.)

Beilsteins Handbuch der organischen Chemie, edited by F. Richter. 4th edn., 2nd suppl., Vol. 28, Part 2. General Sachregister für das Hauptwerk und die Ergänzungswerke I und II, H–Z. Springer-Verlag. 1956. (Presented by the Editor.)

The biochemistry and physiology of bone, edited by G. H. Bourne. Academic Press Inc. 1956.

Geochemistry of iodine; iodine in rocks, minerals, and soils. Annotated bibliography 1825—1954, with review and tables. Chilean Iodine Educational Bureau. 1956. (Presented by the Publishers.)

Statistical mechanics of irreversible change, by R. T. Cox. The Johns Hopkins Press. 1955.

Ergebnisse der exakten Naturwissenschaften, edited by S. Flügge and F. Trendelenburg. Vol. 29. Springer-Verlag. 1956.

Reduction with complex metal hydrides, by N. G. Gaylord. Interscience Publishers Inc. 1956.

Small-angle scattering of *X*-rays, by A. Guinier and G. Fournet. Translation by C. B. Walker. John Wiley & Sons, Inc. 1955.

The chemistry and reactivity of collagen, by K. H. Gustavson. Academic Press Inc. 1956.

The chemistry of tanning processes, by K. H. Gustavson. Academic Press Inc. 1956.

The chemical constitution of natural fats, by T. P. Hilditch. 3rd edn. Chapman & Hall Ltd. 1956.

Proceedings of the International Conference on the Peaceful Uses of Atomic Energy held in Geneva, 1955. Vol. 8. Production technology of the materials used for nuclear energy. United Nations. 1956.

Blood group substances; their chemistry and immunochemistry, by E. A. Kabat. Academic Press Inc. 1956.

Preparation and properties of (inorganic) borates in aqueous solutions, by A. D. Keshan. Academy of Sciences of the Latvian S.S.R. 1955. (Presented by the Publishers.)

Traité de pharmacie chimique, edited by P. Lebeau. 4th edn. 5 vols. Masson et Cie. 1955—56. (Presented by the Publishers.)

Progrès récents de la chromatographie, by E. Lederer. Part 3 Chromatographie sur papier des radioéléments, by M. Lederer. Hermann & Cie. 1956. (Presented by the Publishers.)

Biochemistry and the central nervous system, by H. McIlwain. J. & A. Churchill Ltd. 1955.

Fluidization, edited by D. F. Othmer. Reinhold Publ. Corp. 1956.

Nouveau traité de chimie minérale, edited by P. Pascal. Vol. 1 Généralitiés, air, eau, hydrogène, deutérium, tritium, hélium et gaz inertes, by G. Bouissières, M. Haïssinsky, G. Pannetier, P. Pascal, and R. Viallard. Masson et Cie. 1956. (Presented by the Publishers.)

Gas chromatography, by C. Phillips. Butterworths Scientific Publications. 1956.

Biographisch-literarisches Handwörterbuch der exakten Naturwissenschaften, by J. C. Poggendorff. Vol. VIIa, Part I: A-E. 3. Lieferung. Akademie-Verlag. 1956.

Vapor-plating; the formation of coatings by vapor-deposition techniques, by C. F. Powell, I. E. Campbell, and B. W. Gonser. John Wiley & Sons, Inc. 1955.

Tables de constantes et données numériques. Vol. 6. Constantes sélectionnées pouvoir rotatoire naturel. Part 1. Stéroides, by J.-P. Mathieu and A. Petit. Masson & Cie. 1956. (Presented by the Publishers.)

The electrolytic and chemical polishing of metals in research and industry, by W. J. McG. Tegart. Pergamon Press Ltd. 1956.

Synthetic methods of organic chemistry: an annual survey, by W. Theilheimer. Vol. 10. S. Karger. 1956.

The life of bacteria; their growth, metabolism, and relationships, by K. V. Thimann. Macmillan Co. 1955.

Ullmanns Encyklopädie der technischen Chemie, edited by W. Foerst. Vol. 7. Färberei bis Gastrennung. 3rd edn. Urban & Schwarzenberg. 1956.

Nitroindanedione, by G. Vanag. Academy of Sciences of the Latvian S.S.R. 1954. (Presented by the Publishers.)

British Chemical Engineering, edited by W. E. Dick. 1956, **1**, No. 1 (May). (A new periodical.) Heywood & Co. Ltd.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING SEPTEMBER AND OCTOBER, 1956

LONDON.

Thursday, October **18***th*, **1956**, *at* 7.30 *p.m.*

The following papers will be presented :

"Hydroaromatic Steroid Hormones. Part V. Some D-Homo-18 : 19-bisnorsteroids." By A. J. Birch and Herchel Smith.

"The Reduction of Diphosphorpyridine Nucleotide and some Model Compounds by means of *X*-Rays." By G. Stein and A. J. Swallow.

"By-ways of Synthesis of Cortisone from Hecogenin. Part I. 9-Dehydrohecogenin as Intermediate in Preparation of 11-Oxygenated Compounds (11-Oxotigogenin and 3β-Acetoxy-5α-pregnan-17α-ol-11 : 20-dione). Part II. A Route to 11-Oxygenated Compounds through 11-Bromo-5α-pregnane-3β : 20β-diol-12-one Diacetate." By R. K. Callow and V. H. T. James.

To be held in the Rooms of the Society, Burlington House, W.1.
Abstracts of the Papers may be obtained from the General Secretary.

ABERDEEN.

Friday, October **19***th*, **1956**, *at* 7.30 *p.m.*

Lecture, **The Biochemical Revolution,** by Mr. M. A. Pyke, M.A., B.Sc. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at Marischal College.

BIRMINGHAM.

Friday, October **12***th*, **1956**, *at* 4.30 *p.m.*

Lecture, **Acetylene–Allene Chemistry,** by Professor E. R. H. Jones, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with Birmingham University Chemical Society, to be held in the Chemistry Department, The University.

BRISTOL.

Thursday, October **4***th*, **1956**, *at* 7.0 *p.m.*

Lecture, **On the Nature of Meat,** by Dr. E. H. Callow. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

Thursday, October **18***th*, **1956**, *at* 7.0 *p.m.*

Lecture, **Degradation of Cholesterol and the Origin of its Carbon Atoms from Acetate,** by Dr. G. Popjak. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

Thursday, October 25th, 1956, at 5.15 p.m.

Lecture, **Aromatic Substitution,** by Professor M. J. S. Dewar, M.A., D.Phil. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

CAMBRIDGE.

Monday, October 8th, 1956, at 8.30 p.m.

Lecture, **Amine Oxidation,** by Dr. H. B. Henbest, B.Sc., A.R.C.S., A.R.I.C. To be given in the University Chemical Laboratory, Cambridge.

EDINBURGH.

Thursday, October 18th, 1956, at 7.30 p.m.

Lecture, **An Aspect of Natural Product Chemistry,** by Professor F. S. Spring, D.Sc., Ph.D., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in The Pharmaceutical Society Rooms, York Place, Edinburgh.

EXETER.

Friday, October 26th, 1956, at 5.0 p.m.

Lecture, **Modern Research on Phase Transformations,** by Professor A. R. Ubbelohde, M.A., D.Sc., F.R.S. To be given at the Washington Singer Laboratories, Prince of Wales Road, Exeter.

GLASGOW.

Friday, October 26th, 1956, at 3.30 p.m.

Lecture, **Metal Atoms as Aromatic Systems,** by Dr. J. Chatt, M.A., F.R.I.C. Joint Meeting with the Alchemists' Club and the Andersonian Chemical Society, to be held in Room 24, The Royal Technical College, Glasgow, C.1.

HULL.

Thursday, October 18th, 1956, at 6.0 p.m.

Lecture, **The Separation of Volatile Substances by Gas–liquid Chromatography,** by Dr. A. T. James. To be given in the Organic Chemistry Lecture Theatre, The University.

LEEDS.

Thursday, October 25th, 1956, at 6.30 p.m.

Royal Institute of Chemistry Lecture by Professor W. Bradley, Ph.D., D.Sc., F.R.I.C. Joint Meeting with the Leeds University Chemical Society to be held in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

MANCHESTER.

Friday, October 5th, 1956, at 6.30 p.m.

Lecture, **Corrosion Fatigue,** by Dr. U. R. Evans, M.A., F.R.S. Joint Meeting with the Royal Insitute of Chemistry and the Society of Chemical Industry to be held in the Chemistry Lecture Theatre, The University.

Friday, October 19*th*, 1956, *at* 6.30 *p.m.*

Official Meeting and Lecture, **Recent Studies in the Stereochemistry of Sub-group VIb,** by Dr. S. C. Abrahams, B.Sc., A.R.I.C. To be held at The College of Technology.

Wednesday, October 31*st*, 1956, *at* 6.30 *p.m.*

Meeting for the Reading of Original Papers. To be held at The College of Technology.

NEWCASTLE AND DURHAM.

Tuesday, October 16*th*, 1956, *at* 5.15 *p.m.*

Lecture, **Isotopes in Industry,** by Dr. H. Seligman. Joint Meeting with the Durham Colleges Chemical Society to be held in the Applebey Lecture Theatre, Science Laboratories, The University, Durham.

Friday, October 26*th*, 1956, *at* 5.30 *p.m.*

Bedson Club Lecture, **Modern Inorganic Stereochemistry,** by Professor R. S. Nyholm, D.Sc., Ph.D., A.R.I.C. To be given in the Chemistry Building, King's College, Newcastle upon Tyne. (All Fellows are invited.)

Monday, October 29*th*, 1956, *at* 5.15 *p.m.*

Lecture, **Nucleotide Structure and Function,** by Professor J. Baddiley, D.Sc., Ph.D. Joint Meeting with the Durham Colleges Chemical Society to be given in the Science Laboratories, The University, Durham.

NORTHERN IRELAND.

Friday, September 14*th*, 1956, *at* 7.15 *p.m.*

Lecture, **Air Pollution,** by Dr. A. C. Monkhouse, F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry to be held at Queen's University, Belfast.

Tuesday, October 9*th*, 1956, *at* 7.15 *p.m.*

Lecture, **Chemistry and the Causeway,** by Mr. E. M. Patterson, M.Sc., A.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry to be held at Queen's University, Belfast.

Tuesday, October 30*th*, 1956, *at* 7.45 *p.m.*

Lecture, **Metal Atoms, in Covalent Compounds, as Aromatic Systems,** by Dr. J. Chatt, M.A., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry to be held at Queen's University, Belfast.

NOTTINGHAM AND LEICESTER.

Monday, October 29*th*, 1956, *at* 4.30 *p.m.*

Lecture, **Recent Advances in the Chemistry of Bile Salts,** by Professor G. A. D. Haslewood, D.Sc., Ph.D., F.R.I.C. Joint Meeting with the Chemical Society of The University College, Leicester, to be held at University College, Leicester.

OXFORD.

Monday, October 22*nd*, 1956, *at* 8.15 *p.m.*

Lecture, **Sandwich Complexes,** by Professor G. Wilkinson, Ph.D., A.R.C.S. Joint Meeting with the Oxford University Alembic Club to be held in the Physical Chemistry Laboratory, Oxford.

SHEFFIELD.

Thursday, October **18th**, **1956**, *at* **7.30** *p.m.*

Lecture, **The Chemistry of Vitamin B_{12},** by Professor A. W. Johnson, Ph.D., A.R.I.C. Joint Meeting with Sheffield University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

SOUTHAMPTON.

Friday, October **19th**, **1956**, *at* **5.0** *p.m.*

Lecture, **Steric Hindrance in Analytical Chemistry,** by Dr. H. Irving, M.A., F.R.I.C. Joint meeting with the University Chemical Society and the Royal Institute of Chemistry to be held in the Chemistry Department, The University.

SOUTH WALES.

Monday, October **15th**, **1956**, *at* **5.30** *p.m.*

Lecture, **Some Recent Studies in Relation to Biosynthesis,** by Professor A. J. Birch, D.Sc., D.Phil. To be given in the Department of Chemistry, University College, Cardiff.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
James Bruce Miller (Aberdeen)	Apr. 4th, 1889.	May 30th, 1956.
Charles Proud (Westcliff-on-Sea)	Dec. 2nd, 1909.	May 25th, 1956.
George Bernard Shapiro (Brooklyn)	Feb. 15th, 1951.	Oct. 23rd, 1955.
Emily Gertrude Turner (Rotherham)	Feb. 21st, 1924.	June 14th, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to the following Fellows, who completed 50 years of Fellowship on July 5th, 1956:

Arthur John Berry (Cambridge).
Samuel Shrowder Pickles (Bradford-on-Avon).
William Macro Seaber (London, E.C.3).
Robert Hutchison Turnbull (London, N.W.7).

ACKNOWLEDGMENTS.

The thanks of the Society have been conveyed to Mr. R. B. Colins for a gift of the Society's publications.

LOCAL REPRESENTATIVE—SOUTHAMPTON.

The thanks of the Society for his services have been conveyed to Dr. N. B. Chapman on his retirement as Local Representative for Southampton; Dr. Ishbel G. M. Campbell has been appointed as his successor.

ELECTION OF NEW FELLOWS.

The following 39 candidates were elected Fellows of the Society on July 11th, 1956:

S. Shahabuddin Ahmad.
Thomas Ewart Axford.
Zdenek Bayer.
Paul Emil Bohny.
Donald James Bush.
Bruce Lindsey Cockburn.
John Wilfred Collette.
Thomas Collett-Jones.
John Salvatore Conte.
Terence Guy Corbett.
Robert Munro Cowper.
John Leonard Crew.
David Albert Victor Dendy.
Maung Di.
Alan Dun.
Lennart Eugen Eberson.
David Augustine Harper.
Walter R. Hertler.
Frederick Charles James.
James Joseph Lawler.
Norman Albert Lebel.
Norman Keith Matheson.
Wybe Thomas Nauta.
Eric Nield.
Kenneth Gordon Oldham.
Raymond Walter Olliff.
Gerald Seaton Pope.
John Priestnall Redfern.
Arthur Stanley Rosenberg.
Myron Rosenblum.
Derek Peter Norman Satchell.
Gerald Smolinsky.
Lindsay Anderson Summers.
Colin Ronald Veale.
Richard Arthur Wall.
Peter George Ward.
Peter David Jacob Weitzman.
Mervyn Charles Woods.
Heinrich Zollinger.

TIMES OF SCIENTIFIC MEETINGS IN LONDON.

In the postal ballot of Fellows in the London area and Home Counties, a small majority favoured a continuance of the present arrangements. The Council has accordingly decided that no change should be made.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in November next. All persons who have received grants, and whose accounts have not been declared closed by the Council, are informed that reports must be received by the Society not later than November 1st, 1956.

Applications for grants, to be made on forms available from the General Secretary, must be received on or before November 15th, 1956. Applications from Fellows will receive prior consideration.

THE PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CO-ORDINATION COMPOUNDS.

This publication will contain the papers read at the Amsterdam Conference held on April 28th—May 3rd, 1955, under the auspices of the Royal Netherlands Chemical Society, together with the discussions (*ca.* 400 pages in total). The papers, but not the discussion, will be found in *Rec. Trav. Chim.*, **75**, 557—924, 1956.

Orders for the proceedings can be placed on payment of f. 15.0 (fifteen Netherlands Guilders) to Messrs. N.V. Amsterdamse Bank, Lange Vijverberg 4, The Hague, to the account of the Royal Netherlands Chemical Society.

Those interested are requested to send their orders at their earliest convenience, as only a limited number of copies will be printed. Fellows resident in the United Kingdom should arrange to forward payment through their bankers.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at the University College of North Staffordshire, Keele, Staffordshire, on Monday, July 16th, to Thursday, July 19th, 1956.

Professor H. D. Springall welcomed the Society to Keele.

The President, Professor E. L. Hirst, D.Sc., F.R.S., then took the Chair.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: D. A. Dowden, I. Steltzer, E. R. S. Winter, H. Watts, R. Rudham, B. M. W. Trapnell, K. G. Ashurst, John R. Lewis, P. D. Groves, F. Abbey, T. Mottershead, G. M. Burnett, E. J. Blackman, J. I. Landon, J. P. Jones, John B. Matthews, John M. Thomas, P. White, H. Marsh, Colin Jackson, H. Heaney, Colin Mortimer, James Grigor, M. R. Harris.

SYMPOSIUM.

The Chairman then opened the Symposium on Chemisorption and Professor W. E. Garner took the Chair for the first session entitled "Theory of Chemisorption."

During the next three days four further sessions took place: "Chemisorption on Insulators" under the Chairmanship of Mr. D. A. Dowden, "Chemisorption on Metals" under the Chairmanship of Professor D. D. Eley, "Chemisorption on Carbon" under the Chairmanship of Professor W. F. K. Wynne-Jones, and "Chemisorption on Semiconductors" under the Chairmanship of Dr. F. S. Stone.

At the conclusion of the meeting, Professor Garner expressed his gratitude to the contributors to the Symposium and to the University authorities for hospitality.

Professor H. D. Springall replied and, on behalf of the Society, Dr. J. Chatt thanked both Professor Garner and Professor Springall for their contributions to the success of the meeting.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the Journal *for August, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Anbar, Michael, M.Sc., and Ph.D. (Jerusalem). Israeli. Weizmann Institute of Science, P.O. Box No. 26, Rehovoth, Israel. **Research Chemist.** *Signed by:* M. Halmann, F. S. Klein.

Arotsky, Judah. British. 153, Brocket Way, Chigwell, Essex. Student. *Signed by:* N. B. Chapman, M. C. R. Symons.

Bishop, Derek Charles, B.Sc. (Lond.) British. 26, Sylvan Avenue, Wood Green, London, N.22. Graduate at London University. *Signed by:* John E. Salmon, C. L. Arcus.

Blackadder, David Andrew, B.Sc. (Edin.). British. 315, Iffley Road, Oxford. Research Student. *Signed by:* R. E. Richards, C. N. Hinshelwood.

Bumgardner, Carl Lee, B.A.Sc. (Toronto), Ph.D. (M.I.T.). American. c/o Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama, U.S.A. Research Chemist. *Signed by:* A. Fournier, J. S. Stephenson.

Chiang, Hung-Chen, B.Sc. (Taiwan). Chinese. c/o Mrs. Teildesley, 87, Terry Street, St. Peters, Sydney, Australia. Postgraduate Student of Sydney University. *Signed by:* T. R. Watson, A. V. Robertson.

Darby, Paul William, B.Sc., and Ph.D. (Bris.). British. Queen's Elms, University Road, Belfast, Northern Ireland. Research Fellow at Queen's University, Belfast. *Signed by:* D. Brennan, E. J. Blackman.

Dummel, Robert Joseph, B.S. (San Francisco), M.S. (Stanford). American. 2171, Princeton Avenue, Palo Alto, California, U.S.A. Graduate Student. *Signed by:* M. Look, L. J. Durham.

Eisner, Adrienne Gertrud Adele, D.Phil. (Berlin). Austrian. 27, Blenheim Gardens, London, N.W.2. *Signed by:* R. S. Cahn, K. Lonsdale.

Eric, Bozidar V., B.Sc. (Lond.). Serbian. Plot No. 4, Winfield Estate, Borrowash Road, Spondon, Derby. Research Chemist. *Signed by:* W. C. Paterson, A. G. Catchpole.

Evans, Frederick Peter, B.Sc. and Ph.D. (Wales). British. 81, Stratfield Road, Basingstoke, Hants. Scientific Officer at Atomic Weapons Research Establishment, Aldermaston. *Signed by:* M. W. Roberts, L. V. C. Rees.

Faulkner, Robert Davis, B.S. (Florida), M.S. (Purdue). American. c/o Chemistry Department, Florida State University, Tallahassee, Florida, U.S.A. Graduate Student. *Signed by:* J. E. Lefiler, E. Grunwald.

Fitch, George Roy, B.Sc. (Lond.), A.R.I.C. British. 5A, Waterloo Terrace, Newhampton Road East, Wolverhampton. Assistant Lecturer at Wolverhampton Technical College. *Signed by:* H. Marsh, C. Jackson.

Forsythe, James Horace William, B.Sc. (Q.U.B.). British. 62, Somerton Road, Belfast, N. Ireland. Research Chemist. *Signed by:* C. L. Wilson, R. J. Magee.

Good, William, D.Sc. (Zurich), A.R.I.C., A.R.T.C. British. The Royal Technical College, Glasgow, C.1. Lecturer. *Signed by:* F. S. Spring, J. McLean.

Griffiths, Samuel Thomas, B.Sc. (Wales., A.R.I.C. British. The Associated Ethyl Co., Ltd., Engine Laboratory, Watling Street, Bletchley, Bucks. Research Chemist. *Signed by:* R. O. Gibson, D. B. Clapp.

Harper, Brian John Thomas, B.Sc. (Bris.). British. 30, Hampton Park, Red Land, Bristol, 6. Research Student. *Signed by:* D. Davidson, A. R. Battersby.

Harvey, Frank Reid, B.Sc. (Lond.), A.R.I.C. British. Harleyford Manor, Marlow, Bucks. Lecturer. *Signed by:* C. B. F. Rice, K. S. W. Sing.

Hatfield, Michael Roland, B.A. (Oxon.). British. "Bodiam," Twyford Abbey Road, London, N.W.10. Brewer. *Signed by:* J. C. N. Carroll, J. I. Webb.

Hayward, David Oldham, B.A. (Cantab.). British. 30, Bellefield Avenue, West Derby, Liverpool, 12. Research Student. *Signed by:* A. K. Holliday, B. M. W. Trapnell.

Hickman, John, B.Sc. (Lond.). British. Department of Chemistry, Washington Singer Laboratories, Perry Road, Exeter, Devon. Research Student. *Signed by:* S. J. Gregg, K. Schofield.

Hoppe, Jack Ian, B.Sc. and Ph.D. (Reading). British. 7, Erleigh Road, Reading, Berks. Research Student. *Signed by:* J. E. Prue, E. S. Halberstadt.

Jackson, Ronald Whiteley, M.Sc. (Manc.), Ph.D. (Bris.), A.R.I.C. British. 90, Hayes Chase, West Wickham, Kent. Research Chemist. *Signed by:* W. E. Garner, F. S. Stone.

Johns, Stanley Roy, B.Sc. (New England.). British. University of New England, Armidale, N.S.W. Australia. Student. *Signed by:* V. R. Stimson, N. V. Riggs.

Johnson, George. British. 11, Lakeside Caravan Site, Thorney Mill Road, West Drayton, Middlesex. Chief Chemist at Simoniz (Eng.), Ltd., Iver, Bucks. *Signed by:* F. C. Martin, R. Rowe.

Lawley, Philip Douglas, B.A. (Oxon.), Ph.D. (Nott.). British. 70, Pineapple Road, Amersham, Bucks. Research Chemist. *Signed by:* S. F. D. Orr, E. M. F. Roe.

Layzell, Thomas Richard, British. 8, Bell View, Windsor, Berks. Student. *Signed by:* M. J. S. Dewar, W. J. Hickinbottom.

Leaback, David Herbert, M.Sc. and Ph.D. (Lond.). British. **36,** Aberdare House, Sumner Road, Peckham, London, S.E.15. Assistant in Biochemistry, Institute of Orthopædia. *Signed by:* D. S. P. Patterson, T. F. Slater.

Leberman, Reuben, B.Sc. (Lond.). British. **9/36,** Hopetown Street, London, E.1. Postgraduate Student. *Signed by:* A. P. Mathias, S. P. Datta.

Leigh, William Richard Bruce, B.Sc. (Sydney), A.R.A.C.I. British. c/o C. S. R. Chemicals Pty. Ltd., 1, Mary Street, Rhodes, New South Wales, Australia. Factory Manager. *Signed by:* R. J. W. Le Fèvre, T. Iredale.

Little, Leslie Harry, M.Sc. (Western Australia), A.R.A.C.I. Australian. 16, Pork Street, Cambridge. Research Student. *Signed by:* R. Parsons, D. A. Dowden.

Lovett, John Francis. British. **26,** Spensley Road, Westoning, Bedford. Plant Protection Chemist. *Signed by:* R. de B. Ashworth, J. D. Jones.

Lowe, Peter Albert, B.Sc. (Lond.), A.R.I.C. British. **194,** Kings Road, Ashton-under-Lyne, Lancs. Research Student. *Signed by:* M. R. Harris, A. Holt.

McGregor, William Robert, B.Sc. (Southampton). British. **25,** Ruby Road, Bitterne, Southampton, Hants. Research Student. *Signed by:* N. B. Chapman, G. W. A. Fowles.

McHugh, Dennis Joseph, B.Sc. (Sydney). Australian. **1625,** Pittwater Road, Mona Vale, Sydney, Australia. University Teaching Fellow. *Signed by:* G. W. K. Cavill, S. J. Angyal.

Maggs, Frederick Arthur Pomroy, B.Sc. and Ph.D. (Lond.), F.R.I.C. British. **53,** Westwood Road, Salisbury, Wiltshire. Physical Chemist. *Signed by:* S. J. Gregg, R. M. Barrer.

Miller, Montague. British. Fairholt Lodge, 1a, Fairholt Road, London, N.16. Pharmacist. *Signed by:* L. G. F. Dolley, E. W. Tapley.

Nelson, Samuel Martin, M.Sc. and Ph.D. (Q.U.B.). British. Magdalen College, Oxford. Research Student. *Signed by:* L. E. Sutton, A. D. Buckingham.

Newland, Julian Harold, B.A. (New York). American. 216, Depot Road, Huntington Station, New York, U.S.A. Graduate Assistant, New York University. *Signed by:* R. T. Morrison, R. N. Boyd, B. Arnowich.

Nosworthy, Judith Madeleine, B.A. (Cantab.). British. Physics Department, Medical School, Guys Hospital, London, S.E.1. Research Assistant. *Signed by:* G. A. D. Haslewood, R. J. Bridgwater.

Olah, George Andrew. Hungarian. Budapest XIV, Hungaria krt. 114, Hungary. Research Director. *Signed by:* L. Mester, F. Kovacs.

Owen, Michael Allan. British. 1, Sharp Way, Dartford, Kent. Analytical Chemist. *Signed by:* W. A. Snow, A. H. Thorneloe.

Pickup, Kenneth George, B.Sc. (Liv.). British. **52,** Bridge Road, Liverpool, 18. Research Student. *Signed by:* A. K. Holliday, B. M. W. Trapnell.

Pritchard, John, B.Sc. and Ph.D. (Lond.), A.R.C.S., D.I.C. British. **7,** Ranmore Avenue, Croydon, Surrey. Research Chemist. *Signed by:* F. S. Stone, R. M. Barrer.

Rosenbaum, Jack. British. 2a, Burchell Road, Leyton, E.10, London. Student. *Signed by:* N. B. Chapman, I. G. M. Campbell.

Sandstrom, Jan Olof, Fil.Dr. (Lund.). Swedish. Department of Chemistry, Helgonavagen, Lund, Sweden. Lecturer. *Signed by:* S. Sunner, E. Larsson.

Sharma, Brahama Datta, M.Sc. (Delhi). Indian. c/o Chemistry Department, University of Southern California, Los Angeles 7, California, U.S.A. Student, *Signed by:* J. A. Berson, W. K. Wilmarth.

Smith, Michael, B.Sc. (Dunelm). British. **14,** Links Road, Cullercoats, North Shields, Northumberland. Research Student. *Signed by:* H. Marsh, C. Jackson.

Stark, Bernard Peter, B.A. (Cantab.). British. **36,** Lyndewode Road, Cambridge. Research Student. *Signed by:* A. G. Holmes-Siedle, B. C. Saunders.

Stoward, Peter John. British. Oriel College, Oxford. Undergraduate. *Signed by:* L. A. K. Staveley, B. R. Brown.

Trapp, Orlin Dalton, jun., B.A. (Westmar College). American. Chemistry Department, Iowa State College, Ames, Iowa, U.S.A. Graduate Student. *Signed by:* J. Tanaka, F. T. Fang.

Turvey, James Robert, B.Sc. and Ph.D. (Wales), A.R.I.C. British. "Bronallt," Penrhosgarnedd, Bangor, Caerns. University Lecturer. *Signed by:* J. E. McKail, W. R. Angus.

Urch, David Selway, B.Sc. (Lond.). British. **36,** Windermere Road, Muswell Hill, London, N.10. Student. *Signed by:* M. J. S. Dewar, T. Mole.

von Bertele, Emy Marcelline Elizabeth, B.Sc. (Lond.). Austrian. 6, Warner Road, Purley, Surrey. Technical Assistant. *Signed by:* M. M. Coombs, F. Bowyer.

Wasserman, Edel, M.A. (Harvard). American. Converse Laboratory, Harvard University, Cambridge 38, Mass., U.S.A. Student. *Signed by:* R. L. Autrey, H. Richey.

Williamson, Elizabeth Jessie, B.Sc. (New England). British. **13,** Tilehurst Road, Reading, Berks. Research Chemist. *Signed by:* J. A. Radley, M. L. McGlashan.

Yadava, Brijnandan Prasad, M.Sc. and Ph.D. (Lucknow). Indian. Department of Physical Chemistry, Free School Lane, Cambridge. Research Student. *Signed by:* E. A. Moelwyn-Hughes, J. N. Agar.

APPERTAINING TO FELLOWS RESIDENT ABROAD.

Ashraf, Muhammed, M.Sc. (Punjab.). Pakistani. Government College Kobat, West Pakistan. Lecturer. *Signed by:* M. I. D. Chughtai.

Blumenfeld, Solly, Dipl.Pharm. (SouthAfrica). South African. c/o Barclays Bank (West End Foreign Branch), 1, Pall Mall East, London, S.W.1. Pharmacist. *Signed by:* J. L. Ratner.

Dailey, Benjamin Peter, M.A. and Ph.D. (Univ. of Texas). American. O.N.R. 429, Oxford Street, London, W.1. Scientific Liasion Officer. *Signed by:* E. R. S. Winter.

Gordon, Harry Michael, Dipl.Pharm. (South Africa), M.P.S. South African. c/o Barclays Bank (D.C.O.), 1, Cockspur Street, London, S.W.1. Pharmaceutical Chemist. *Signed by:* J. L. Ratner.

Gorin, George, A.B. (Brooklyn Coll.), M.A. and Ph.D. (Princeton Univ.). American. Department of Chemistry, Oklahoma A and M College, Stillwater, Oklahoma, U.S.A. Assistant Professor. *Signed by:* O. C. Dermer.

Hino, Tohru, B.Pharm. (Univ. of Tokyo). c/o Department of Chemistry, University of Washington, Seattle 5, Washington, U.S.A. Research Assistant. *Signed by:* H. J. Dauben, jun.

Hojo, Nobumasa. Japanese. C/o Textile Dept., Shinshu University, Ueda, Japan. Assistant Professor. *Signed by:* O. Simamura.

Markowitz, Samuel S., B.S. (Rensslaer Poly. Inst.), M.A. and Ph.D. (Princeton Univ.). American. Department of Chemistry, Brookhaven National Library, Upton, Long Island, New York, U.S.A. Postgraduate. *Signed by:* N. Sutin.

Tewari, Swarup Narain, M.Sc. and D.Phil. (Allahabad), A.R.I.C. Indian. "Hill House." 84, Civil Lines, Agra, India. Assistant to Chemical Examiner and Government Analyst. *Signed by:* M. C. Thoung.

Willson, Clyde DeClifford, A.B. (Univ. of Calif.). American. 2223a, Roosevelt Avenue, Berkeley 3, California, U.S.A. Student. *Signed by:* E. J. Behrman.

Yan, John Si Chiu, B.Sc. (McKinley-Roosevelt Univ.). Chinese. 83, Tai Nam Street, 3rd Floor, Monkok, Kowloon, Hong Kong. Senior Science Master. *Signed by:* J. M. M. Che.

Zerner, Ernst, Ph.D. (Univ. of Vienna). American. c/o Argus Chemical Corporation, 633, Court Street, Brooklyn 31, New York, U.S.A. Consulting Chemist. *Signed by:* C. G. Overberger.

• Reduced subscription.

PAPERS ACCEPTED

(List of Papers accepted between June 22nd and August 3rd, 1956, for publication in the *Journal.*)

"Application of the Bruckner method to the synthesis of phenanthridine derivatives." By T. R. Govindachari, K. Nagarajan, B. R. Pai, and N. Arumugam.

"The preparation and manipulation of molybdenum hexafluoride." By T. A. O'Donnell.

"The surface chemistry of germanium. Part I. Chemical effects at *pn*-junctions." By J. I. Carasso and I. Stelzer.

"Barringtogenol and barringtogenic acid, two new triterpenoid sapogenins. Part I." By R. Anantaraman and K. S. Madhaven Pillai.

"Studies in aromatic nucleophilic replacement. Part VI. Some effects of alkyl groups." By C. W. L. Bevan, T. O. Fayiga, and J. Hirst.

"The effects of substituents on the rates of hydrolysis of some organophosphorus compounds. Part I. Rates in alkaline solution." By D. F. Heath.

"The effects of substituents on the rates of hydrolysis of some organophosphorus compounds. Part II. Rates in neutral solution." By D. F. Heath.

"Effect of added hydroxy-compounds on the association of benzoic acid." By Winifred G. Wright.

"The dissociation pressure of cadmium oxide." By I. G. F. Gilbert and J. A. Kitchener.

"The free energy of formation of zinc aluminate." By I. G. F. Gilbert and J. A. Kitchener.

"The free energy of formation of zinc ferrite." By I. G. F. Gilbert and J. A. Kitchener.

"The strengths of arylmethanols as secondary bases." By V. Gold.

"Steric effects in electronic spectra." By J. N. Murrell.

"Magnetic properties of some metal carboxylates." By R. C. Herron and R. C. Pink.

"Curare and related topics. Part II. The structure and anomalous optical rotation of *iso*chondrodendrine." By John A. D. Jeffreys.

"A theoretical investigation of the chemical reactivity of benziminazole." By R. D. Brown and M. L. Heffernan.

"Experiments on the synthesis of 3 : 4- and 5 : 6-benzophenanthridines." By B. Mills and K. Schofield.

"Experiments with 1 : 2 : 3 : 4-tetrahydro-3-methylquinazoline and related compounds." By A. R. Osborn and K. Schofield.

"The gum component of olibanum." By H. El-Khadem and M. M. Megahed.

"Antituberculosis agents. Part II. Dehydrobromination products and related bases derived from bis-2 : 3-dibromopropyl sulphide." By D. Edwards and J. B. Stenlake.

"Phthalazines. Part I. Re-investigation of the preparation of phthalazines by cyclodehydration of acylhydrazones." By H. J. Rodda and P. E. Rogasch.

"Molecular polarisation in ternary systems comprising benzene, pyridine, and an alcohol." By D. Cleverdon, G. B. Collins, and J. W. Smith.

"Solutions in sulphuric acid. Part XX. Cryoscopic measurements on some aromatic sulphides, sulphoxides, and sulphones." By R. J. Gillespie and R. C. Passerini.

"Polyazanaphthalenes. Part IV. Further derivatives of 1 : 3 : 5- and 1 : 3 : 8-triazanaphthalene." By V. Oakes and H. N. Rydon.

"Intramolecular acylation. Part I. Ring closure of some β-(7-alkyl-1-naphthyl)-propionic acids." By A. J. M. Wenham and J. S. Whitehurst.

"The Beckmann rearrangement of *cyclo*pentanone oxime." By (Mrs.) T. Stephen and Henry Stephen.

"The preparation of aliphatic aldehydes and ketones from lithium alkyls and dimethylamides." By E. A. Evans.

"Some degradation products of fumagillin." By Justus K. Landquist.

"Vibrational frequency correlations in heterocyclic molecules. Part II. Infrared spectra and structure of oxindole and related compounds." By A. E. Kellie, D. G. O'Sullivan, and P. W. Sadler.

"Four-, five-, and six-covalent palladium(II) complexes with a ditertiary arsine." By C. M. Harris and R. S. Nyholm.

"Researches on polyenes. Part IV. The ω-*p*-methoxyphenylpolyene aldehydes and their absorption spectra." By D. Marshall and M. C. Whiting.

"The viscosity and intermolecular potential of silicon tetrafluoride." By C. P. Ellis and C. J. G. Raw.

"Studies in the synthesis of cortisone. Part XIII. The epimeric 3β : 7-dihydroxyergost-22-en-11-ones." By J. Elks and G. H. Phillipps.

"Studies in the synthesis of cortisone. Part XIV. Acetylhydrazones and azines of steroidal ketones." By J. Elks and G. H. Phillipps.

"Studies in the synthesis of cortisone. Part XV. Improvements in the conversion of hecogenin into 3β : 12β-diacetoxy-5α : 25*D*-spirostan-11-one and a study of the isomeric 11 : 12-ketols." By J. Elks, G. H. Phillipps, T. Walker, and L. J. Wyman.

"Studies in the synthesis of cortisone. Part XVI. A new method of preparing 11-oxotigogenin." By J. H. Chapman, J. Elks, G. H. Phillipps, and L. J. Wyman.

"Studies in the synthesis of cortisone. Part XVII. The bromination of cholestan-3-one." By C. W. P. Crowne, R. M. Evans, G. F. H. Green, and A. G. Long.

"Studies in the synthesis of cortisone. Part XVIII. The preparation of cortisone esters from 4 : 5α-dihydroxycortisone." By R. M. Evans, J. C. Hamlet, J. S. Hunt, P. G. Jones, A. G. Long, J. F. Oughton, L. Stephenson, T. Walker, and B. M. Wilson.

"The thermal degradation of polymethacrylonitrile. Part I. Separation of coloration and depolymerization reactions." By N. Grassie and I. C. McNeill.

"The preparation of some dimeric *sec.*-aminoboron dihalides." By O. C. Musgrave.

"Studies in *cyclo*hexane stereochemistry. Part IV. Some secondary tertiary 1 : 2-diols." By P. R. Jefferies and B. Milligan.

"Studies in *cyclo*hexane stereochemistry. Part V. Infrared spectra and conformations of stereoisomeric 1 : 2-diols." By A. R. H. Cole and P. R. Jefferies.

"Acylation and allied reactions catalysed by strong acids. Part XV. Some reactions of simple alkyl perchlorates." By H. Burton, D. A. Munday, and P. F. G. Praill.

" Organic sulphur compounds. Part I. The structure of anthra-9 : 10-quinone-1-sulphenic acid, its derivatives, and analogues." By J. A. Barltrop and K. J. Morgan.

" The constitution of a xylan from Norway spruce (*Picea excelsa*)." By G. O. Aspinall and (Miss) Mary E. Carter.

" The ultraviolet-light absorption of 3-*O*-methylglycerosazone." By J. C. P. Schwarz and (in part) Maureen Finnegan.

" Picrotoxin and tutin. Part VIII." By R. B. Johns, S. N. Slater, and R. J. Woods (with, in part, D. Brasch and Roy Gee).

" A kinetic study of the alkaline hydrolysis of some aliphatic esters." By J. D. R. Thomas and H. B. Watson.

" Experiments on the synthesis of the pyrethrins. Part XI. Synthesis of *cis*-pyrethrolone and pyrethrin-I : introduction of the *cis*-penta-2 : 4-dienyl system by selective hydrogenation." By L. Crombie, S. H. Harper, and F. C. Newman.

" Synthetic and oxidative studies in the polyhydroxydiphenyl series. Part II. 5 : 6-Dichloro-2 : 3-dihydroxydiphenyl." By J. Malcolm Bruce and F. K. Sutcliffe.

" Synthetic and oxidative studies in the polyhydroxydiphenyl series. Part III. 2 : 3-Dihydroxy-5 : 6-dimethyldiphenyl." By J. Malcolm Bruce and F. K. Sutcliffe.

" The chemistry of extractives from hardwoods. Part XXVII. The structure of terminolic acid." By F. E. King and T. J. King.

" *Aconitum* and *Delphinium* alkaloids. Part III. Some rearrangements in the delpheline and lycoctonine series. A monobasic dicarboxylic acid." By R. C. Cookson and M. E. Trevett.

" The kinetics of hydrogen isotope exchange reactions. Part VI. The reactivity of anisole in aqueous and non-aqueous acidic media." By D. P. N. Satchell.

" Triad prototropic systems. Part IV. The effect of substituents on the mobility of the azomethinecarboxylic acids derived from ketones." By F. G. Baddar and Sayed A. M. Sherif.

" An approach to the synthesis of veratramine. Some derivatives of 2 : 3-dihydroxynaphthalene." By F. H. Howell and D. A. H. Taylor.

" The decomposition of arylazotriarylmethanes." By G. L. Davies, D. H. Hey, and Gareth H. Williams.

" Raman spectrum of the tetrachlorogallate ion ($GaCl_4^-$) in aqueous solution." By L. A. Woodward and A. A. Nord.

" Raman spectrum and constitution of fused gallium dichloride." By L. A. Woodward, G. Garton, and H. L. Roberts.

" The constitution of a wheat-straw hemicellulose." By G. O. Aspinall and Eric G. Meek.

" Organic complex-forming agents for metals. Part III. Compounds containing the *o*-hydroxyphenylphosphine oxide group." By J. Kennedy, E. S. Lane, and J. L. Willans.

" The crystal and molecular structure of thianthren." By H. Lynton and (in part) E. G. Cox.

" The simple fluorides of iridium, including the new trifluoride." By P. L. Robinson and G. J. Westland.

" Reduction of amides by lithium borohydride." By M. Davis.

" The chemistry of extractives from hardwoods. Part XXVIII. The occurrence of 3 : 5 : 3′ : 4′-tetrahydroxy- and 3 : 4 : 5 : 3′ : 5′-pentahydroxy-stilbene in *Vouacapoua* species." By F. E. King, T. J. King, D. H. Godson, and L. C. Manning.

" Vapour–liquid equilibrium data for the benzene–fluorobenzene system." By R. E. Banks and W. K. R. Musgrave.

" Nuclear resonance spectra and the structures of the mono- and the di-hydrate of boron trifluoride." By P. T. Ford and R. E. Richards.

" The thermal decomposition of *cyclo*pentyl bromide." By S. J. W. Price, R. Shaw, and A. F. Trotman-Dickenson.

" Flavogallol." By J. Grimshaw and R. D. Haworth.

" The constitution of conessine. Part IX. Further studies with steroidal amines related to conessine." By R. D. Haworth, L. H. C. Lunts, and J. McKenna.

"Aromatic substitution. Part II. Nitration of aromatic compounds with nitronium tetrafluoroborate and other stable nitronium salts." By G. OLÁH, S. KUHN, and A. MLINKÓ.

"A new synthesis of 3-hydroxy-1 : 2-benzofluorene." By NEIL CAMPBELL and ENGELBERT CIGANEK.

"Structure and stereochemistry of tazettine." By T. IKEDA, W. I. TAYLOR, Y. TSUDA, S. UYEO, and H. YAJIMA.

"Wessely–Moser rearrangement of chromonols and flavonols." By (MISS) D. M. DONNELLY, (MRS.) E. M. PHILBIN, and T. S. WHEELER.

"Oxidation by nitrous and nitric acid. Part IV. Spectroscopic investigation of the equilibrium between NO^+ and nitrous acid in aqueous perchloric acid." By K. SINGER and (MISS) P. A. VAMPLEW.

"A new synthesis of 2 : 3 : 5 : 6-substituted 4-pyrimidones." By BENJAMIN STASKUN and HENRY STEPHEN.

"The chemistry of gum labdanum. Part I. Some acidic constituents." By J. D. COCKER, T. G. HALSALL, and (in part) A. BOWERS.

"The chemistry of gum labdanum. Part II. The structure of labdanolic acid." By J. D. COCKER and T. G. HALSALL.

"The formation of nitrosochlorides and nitrosates." By N. THORNE.

"Dielectric polarisation studies of the formation of hydrogen-bond complexes by alcohols." By (the late) A. H. BOUD and J. W. SMITH.

"Steroids. Part XI. The 3 : 5-*cyclo*steroid rearrangement of dehydroergosteryl toluene-*p*-sulphonate." By W. R. NES and C. W. SHOPPEE.

"The halogenation of phenolic ethers and anilides. Part XVIII. A kinetic method for the determination of the *ortho* : *para* ratios in aromatic ethers." By BRYNMOR JONES and EILEEN N. RICHARDSON.

"Thermal cyclization of *o*-aroyloxyacetoarones. Part III. Synthesis in the chromone series." By T. M. O'TOOLE and T. S. WHEELER.

"Fission of esters of carboxylic acids by boron trichloride." By W. GERRARD and M. A. WHEELANS.

"Derivatives of thionaphthen. Part II. Thionaphthen derivatives formed by cyclisation of acetonyl aryl sulphides and aryl phenacyl sulphides." By J. E. BANFIELD, W. DAVIES, N. W. GAMBLE, and S. MIDDLETON.

"The preparation and characterising constants of the phenylboron chlorides." By E. W. ABEL, S. H. DANDEGAONKER, W. GERRARD, and M. F. LAPPERT.

"(+)-β-Aminobutyric acid; the correlation of configuration with that of α-amino-acids." By K. BALENOVIĆ, N. BREGANT, and D. CERAR.

"Thiadiazoles. Part IV. The oxidation of *N*-(aroylamidino)thioureas." By FREDERICK KURZER.

"Two hypothetical metabolites of paludrine." By R. M. ACHESON and N. F. TAYLOR.

"Tetronic acids and related compounds. Part II. The synthesis of (±)-carolinic acid." By L. J. HAYNES, J. R. PLIMMER, and (in part) A. H. STANNERS.

"Lactones. Part IV. A new preparation of 7-ethoxy-6-methoxyphthalide." By W. R. LOGAN and G. T. NEWBOLD.

"Some experiments with *cyclo*pentanones." By R. M. ACHESON.

"20ξ-Hydroxycholesterol." By VLADIMIR PETROW and (MRS.) ISOBEL A. STUART-WEBB.

"Bisquaternary ammonium salts. Part II. Salts of 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid." By W. G. LEEDS and R. SLACK.

"Syntheses in the quinazolone series. Part IV. The conversion of *N*-aroylorthanilamides into 2-arylquinazol-4-ones." By HENRY STEPHEN and (the late) GEORGE WADGE.

"The partial hydrolysis of dialkyl esters of 4-hydroxy*iso*phthalic acid." By J. M. Z. GLADYCH and E. P. TAYLOR.

"The synthesis of 1 : 2 : 7 : 8-tetrahydro-3-methoxy- and 1 : 2 : 7 : 8-tetrahydro-3 : 10-dimethoxy-chrysene." By J. F. COLLINS and HERCHEL SMITH.

"Attempts at the Meyer–Schuster rearrangement on 2-ethynyl-2-hydroxy*cyclo*hexanone." By (MISS) M. E. MCENTEE, A. R. PINDER, HERCHEL SMITH, and R. E. THORNTON.

" Ionophoresis of carbohydrates. Part IV. Separations of carbohydrates on fibreglass sheets." By E. J. BOURNE, A. B. FOSTER, and P. M. GRANT.

" Studies of sultones." By (MRS.) E. M. PHILBIN, E. R. STUART, R. F. TIMONEY, and T. S. WHEELER.

" Curvularin. Part I. Isolation and partial characterisation of a metabolic product from a new species of *Curvularia*." By O. C. MUSGRAVE.

" Wesseley–Moser rearrangement with xanthones." By (MRS.) E. M. PHILBIN, J. SWIRSKI, and T. S. WHEELER.

" Bisdiguanides having antibacterial activity." By F. L. ROSE and G. SWAIN.

" Further experiments on the epoxidation of steroids." By O. K. SEWELL, J. H TURNBULL, and W. WILSON.

" The preparation and characterisation of *o*-bromophenylmagnesium bromide." By HARRY HEANEY, FREDERICK G. MANN, and IAN T. MILLAR.

" The sulphates and selenate of polonium." By K. W. BAGNALL and J. H. FREEMAN.

" The reaction of ammonium acetate with β-hydroxy-αα-dimethylpropaldehyde." By J. F. CAVALLA.

" Compounds derived from cholestenone." By G. D. MEAKINS and O. R. RODIG.

" Structural chemistry of the alkoxides. Part VIII. Isomeric butoxides and pentyloxides of niobium." By D. C. BRADLEY, B. N. CHAKRAVARTI, and W. WARDLAW.

" Tetronic acids and related compounds. Part III. The Claisen ester condensation of ethyl 2'-tetrahydropyranyloxyacetate." By L. J. HAYNES and J. R. PLIMMER.

" Acyl *iso*thiocyanates. Part I. The synthesis of esters of *N*-acyldithiocarbamic acids." By D. T. ELMORE, J. R. OGLE, and (in part) (MRS.) W. FLETCHER and P. A. TOSELAND.

" The lability of 1 : 4 : 6-triazanaphthalene." By ADRIEN ALBERT and CHRISTIAN PEDERSEN.

" Friedel–Crafts acylation and alkylation. A comparison of inter- and intra-molecular processes." By G. BADDELEY and R. WILLIAMSON.

" Amino-sugars and related compounds. Part I. Observations on the deamination of D-glucosamine hydrochloride." By B. C. BERA, A. B. FOSTER, and M. STACEY.

" Pteridine studies. Part X. Pteridines with more than one hydroxy- or amino-group." By ADRIEN ALBERT, J. H. LISTER, and CHRISTIAN PEDERSEN.

" The position of the tertiary hydroxyl group in agapanthagenin." By G. E. A. MATHEW and (MRS.) T. STEPHEN.

" The synthesis of α- and β-phenyladipic acids." By K. BUTLER and G. P. ELLIS.

" Synthesis of ' 6-succinoaminopurine ' [6-(1 : 2-dicarboxyethylamino)purine]." By J. BADDILEY, J. G. BUCHANAN, F. J. HAWKER, and J. E. STEPHENSON.

" Cytidine diphosphate ribitol from *Lactobacillus arabinosus*." By J. BADDILEY, J. G. BUCHANAN, B. CARSS, and A. P. MATHIAS.

" 2-Acyl derivatives of cyclic 1 : 3-diones. Part IV. The structure of dehydroleptospermone." By W. R. CHAN and C. H. HASSALL.

" Researches on acetylenic compounds. Part LIV. The preparation and synthetical applications of ethynylmagnesium bromide." By E. R. H. JONES, L. SKATTEBÖL, and M. C. WHITING.

ADDITIONS TO THE LIBRARY

Proceedings of the American Society for Testing Materials. **1955**, Vol. **55**. American Society for Testing Materials. **1956**.

Quelques aspects généraux de la science des macromolécules; a symposium held by the Centre National de la Recherche Scientifique, at Strasbourg, **1954**. Centre National de la Recherche Scientifique. **1955**.

La chimie de hautes temperatures; a symposium held by the Centre National de la Recherche Scientifique, at Paris, **1954**. Centre National de la Recherche Scientifique. **1955**.

The proceedings of the conference on oxidation processes held in Amsterdam, **1954**. (*Chemical Engineering Science*, **1954**, Vol. **3**, Special Supplement.) Pergamon Press Ltd. **1954**.

Physiologische Chemie: ein Lehr- und Handbuch für Arzte, Biologen und Chemiker, edited by B. Flaschenträger and E. Lehnartz. Vol. **2**. Der Stoffwechsel, Part **2a**. Springer. **1956**.

La resonance paramagnetique nucleaire. Moments dipolaires et quadripolaires, edited by P. Grivet. Centre National de la Recherche Scientifique. **1955**.

Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, held in Geneva, **1955**. Vol. **12**. Radioactive isotopes and ionizing radiations in agriculture, physiology, and biochemistry. United Nations. **1956**.

Proceedings of the Third International Congress of Biochemistry, Brussels, **1955**, edited by C. Liébecq. Academic Press Inc. **1956**.

Liquid metals handbook. Sodium (NaK) suppl., edited by C. B. Jackson. **3rd** edn. U.S. Atomic Energy Commission. **1955**.

Notes on some members of the Hanckwitz family in England. (*Annals of Science*, **1955**, Vol. **11**, No. **1**.) By R. E. W. Maddison. Taylor and Francis, Ltd. **1955**. (Presented by the Author.)

Analytical standards for M & B brand laboratory chemicals and reagents, **1956**. 5th edn. May & Baker Ltd. **1956**. (Presented by the Publishers.)

Methods of biochemical analysis, edited by David Glick. Vol. **3**. Interscience Publishers Inc. **1956**.

Organic analysis; edited by J. Mitchell, jun., I. M. Kolthoff, E. S. Proskauer, and A. Weissberger. Vol. **2**. Interscience Publishers, Inc. **1954**.

Modern chemical processes: a series of articles describing chemical manufacturing plants, by the Editors of *Industrial and Engineering Chemistry*. Vol. **4**. Reinhold Publ. Corp. **1956**.

Advances in enzymology and related subjects of biochemistry, edited by F. F. Nord. Vol. **17**. Interscience Publishers, Inc. **1956**.

An introduction to crystallography, by F. C. Phillips. 2nd edn. Longmans Green and Co. **1956**. (Presented by the Publishers.)

Irradiation colours and luminescence; a contribution to mineral physics, by K. Przibram. Translated and revised by J. E. Caffyn. 1st English Edn. Pergamon Press, Ltd. **1956**. (Presented by the Publishers.)

Les colles industrielles, by A. Rivat-Lahousse. Dunod. **1956**. (Presented by the Publishers.)

Some aspects of the crystallization of high polymers, by G. Schuur. Rubber-Stichting, Delft. **1955**.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W. University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, M.A., D.Sc., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
,,	G. D. Meakins, M.A., D.Phil., Chemistry Department, The University, Manchester, 13.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham and Leicester	T. J. King, B.Sc., M.A., D.Phil., Chemistry Department, The University, University Park, Nottingham.
,,	E. R. A. Peeling, B.Sc., Ph.D., University College, Leicester.
Oxford.	R. E. Richards, M.A., D.Phil., Lincoln College, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A.R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	Miss Ishbel G. M. Campbell, B.Sc., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.
,,	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff.

PROCEEDINGS
OF THE
CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING NOVEMBER, 1956

LONDON.

Thursday, November 1st, 1956, at 2.30 p.m. and 7.30 p.m.

Symposium, **Newer Interpretations of Reactions and Structure in Carbohydrate Chemistry,** arranged by Dr. G. R. Barker. To be held in the large Chemistry Lecture Theatre, University College, Gower Street, London, W.C.1. (Full details will be circulated.)

Thursday, November 15th, 1956, at 7.30 p.m.

Meeting for the Reading of Original Papers specially arranged to commemorate the 70th Birthday of Sir Ian Heilbron. To be held in the Rooms of the Society, Burlington House, London, W.1.

ABERDEEN.

Friday, November 9th, 1956, at 7.30 p.m.

Lecture, **An Aspect of Conformational Analysis,** by Professor D. H. R. Barton, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

Friday, November 23rd, 1956, at 7 p.m.

Official Meeting and Tilden Lecture, **Physical Properties of High Polymers in Relation to their Chemical Structures,** by Professor G. Gee, M.Sc., Ph.D., F.R.S. To be held in the Chemistry Department, The University.

BIRMINGHAM.

Friday, November 16th, 1956, at 4.30 p.m.

Lecture, **Topology and Chemistry,** by Dr. A. F. Wells, M.A. Joint Meeting with Birmingham University Chemical Society to be held in the Chemistry Department, The University.

Friday, November 30th, 1956, at 4.30 p.m.

Lecture, **Hydrocarbon Compounds of the Transition Metals,** by Professor G. Wilkinson, Ph.D., A.R.C.S. Joint Meeting with Birmingham University Chemical Society to be held in the Chemistry Department, The University.

BRISTOL.

Thursday, November 1st, 1956, at 7 p.m.

Tilden Lecture, **Physical Properties of High Polymers in Relation to their Chemical Structure,** by Professor G. Gee, M.Sc., Ph.D., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

Thursday, November **15th, 1956,** *at* 5.30 *p.m.*

Social Evening. **Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry to be held in the Senior Common Room, The University.**

Friday, November **16th, 1956,** *at* 5 *p.m.*

Lecture, **Overcrowded Molecules,** by Professor C. A. Coulson, M.A., D.Sc., Ph.D., F.R.S. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday, November **22nd, 1956,** *at* 5.15 *p.m.*

Lecture, **Acetylene–Allene Chemistry,** by Professor E. R. H. Jones, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday, November **22nd, 1956,** *at* 7 *p.m.*

Lecture, **Plastics from Petroleum,** by Mr. R. W. King. Joint Meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, and the Plastics Institute, to be held at the Technical College, Brunswick Road, Gloucester.

Thursday, November **29th, 1956,** *at* 5.15 *p.m.*

Lecture, **Science in the Detection of Crime,** by Dr. J. B. Firth, C.B.E., F.R.I.C. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

CAMBRIDGE.

Friday, November **9th, 1956,** *at* 8.30 *p.m.*

Lecture, **Atomic Radiation and Polymers,** by Dr. A. Charlesky. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Lensfield Road.

Friday, November **16th, 1956,** *at* 8.30 *p.m.*

Lecture, **Solutions in Sulphuric Acid,** by Dr. R. J. Gillespie, B.Sc. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Lensfield Road.

Monday, November **26th, 1956,** *at* 8.30 *p.m.*

Lecture, **Aromatic Detrimethylsilylation—Some New Electrophilic Aromatic Substitutions,** by Dr. C. Eaborn, B.Sc., A.R.I.C. To be given in the University Chemical Laboratory, Lensfield Road.

Friday, November **26th, 1956,** *at* 8.30 *p.m.*

Lecture, **Sorption of Vapours in Crystals,** by Professor R. M. Barrer, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Lensfield Road.

EDINBURGH.

Thursday, November **22nd, 1956,** *at* 7.30 *p.m.*

Lecture, **Polymerisation in Heterogeneous Systems,** by Professor C. E. H. Bawn, C.B.E., Ph.D., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the North British Station Hotel.

EXETER.

Friday, November 30th, 1956, at 5 p.m.

Lecture, **Non-benzenoid Aromatic Systems,** by Professor Wilson Baker, D.Sc., Ph.D., F.R.I.C., F.R.S. To be given in the Washington Singer Laboratories, Prince of Wales Road.

GLASGOW.

Wednesday, November 7th, 1956, at 4 p.m.

Lecture, **The Structure of Vitamin B_{12},** by Mrs. D. M. Hodgkin, M.A., Ph.D., F.R.S. Joint Meeting with The Alchemists' Club to be held in the Chemistry Department, The University.

Friday, November 16th, 1956, at 7.15 p.m.

Lecture, **The Hydrogen Isotope Effect in Reaction Kinetics,** by Mr. R. P. Bell, M.A., F.R.S. To be given in the Chemistry Department, The University.

HULL.

Thursday, November 29th, 1956, at 7.30 p.m.

Lecture, **The Steric Control of Chemical Reactivity,** by Dr. G. Baddeley, D.Sc., Ph.D., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry to be held in the Organic Chemistry Lecture Theatre, The University.

IRISH REPUBLIC.

Friday, November 2nd, 1956, at 7.45 p.m.

Lecture, **The Birth and Death of Free Radicals in Polymerisation,** by Dr. C. H. Bamford, M.A., A.R.I.C. Joint Meeting with the Werner Society to be held in the Chemistry Department, Trinity College, Dublin.

LEEDS.

Monday, November 12th, 1956, at 6.30 p.m.

Royal Institute of Chemistry Lecture, **Determination of Alcohol in Blood and Urine of Drunken Drivers and the Interpretation Thereof,** by Dr. D. W. Kent Jones, B.Sc., F.R.I.C. To be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

Thursday, November 15th, 1956, at 6.30 p.m.

Lecture, **Tropylium,** by Professor M. J. S. Dewar, M.A., D.Phil. Joint Meeting with the Leeds University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

LIVERPOOL.

Thursday, November 1st, 1956, at 5 p.m.

Lecture, **Chemistry at Extreme Temperatures,** by Professor G. Porter, M.A., Ph.D. Joint Meeting with the University Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the British Association of Chemists, to be held in the Chemistry Lecture Theatre, The University.

MANCHESTER.

Wednesday, November 14th, 1956, at 6.30 *p.m.*

Lecture, **Recent *X*-ray Structural Determinations in Glasgow,** by Professor J. M. Robertson, Ph.D., D.Sc., F.R.I.C., F.R.S. To be given at the College of Technology.

NEWCASTLE AND DURHAM.

Friday, November 9th, 1956, at 4 p.m.

Meeting for the Reading of Original Papers. To be held in the Chemistry Building, King's College, Newcastle upon Tyne, 1.

Monday, November 12th, 1956, at 5.15 p.m.

Lecture, **Organic Semi-conductors,** by Professor D. D. Eley, M.Sc., Ph.D. Joint Meeting with the Durham Colleges Chemical Society to be held in the Science Laboratories, The University, Durham.

Friday, November 16th, 1956, at 5.30 p.m.

Bedson Club Lecture, **The Chemistry of Some Naturally Occurring Polyacetylenes,** by Professor B. Lythgoe, M.A., Ph.D., F.R.I.C. To be given in the Chemistry Building, King's College, Newcastle upon Tyne, 1. (All Fellows are invited.)

Monday, November 26th, 1956, at 5.15 p.m.

Lecture, **The Mechanics of Steric Hindrance,** by Professor C. K. Ingold, D.Sc., F.R.I.C., F.R.S. Joint Meeting with the Durham Colleges Chemical Society to be held in the Applebey Lecture Theatre, Science Laboratories, The University, Durham.

NORTHERN IRELAND.

Thursday, November 15th, 1956, at 7.15 p.m.

Lecture, **Recent Advances in Acetylene Chemistry,** by Professor R. A. Raphael, D.Sc., D.I.C., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at The Queen's University, Belfast.

NORTH WALES.

Thursday, November 8th, 1956, at 5.45 p.m.

Lecture, **Allene Chemistry,** by Professor E. R. H. Jones, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the University College of North Wales Chemical Society to be held in the Department of Chemistry, University College of North Wales, Bangor.

NOTTINGHAM AND LEICESTER.

Thursday, November 1st, 1956, at 4.45 p.m.

Lecture, **Elaboration Products of Eucarvone,** by Professor R. A. Raphael, D.Sc., D.I.C., F.R.I.C. Joint Meeting with Nottingham University Chemical Society to be held in the Lecture Theatre, Chemistry Department, The University, Nottingham.

Monday, November 19th, 1956, at 4.30 p.m.

Lecture, **The Structure of Vitamin B_{12},** by Mrs. D. M. Hodgkin, M.A., Ph.D., F.R.S. Joint Meeting with the Chemical Society of the University College of Leicester to be held at University College, Leicester.

Tuesday, November 27th, 1956, at 4.45 p.m.

Lecture, **Mechanism of Solid-state Reactions and the Structure of the Solid State,** by Professor W. E. Garner, C.B.E., D.Sc., F.R.S. Joint Meeting with Nottingham University Chemical Society to be held in the Lecture Theatre, Chemistry Department, The University, Nottingham.

OXFORD.

Monday, November 5th, 1956, at 8.15 p.m.

Lecture, **Organometallic Compounds,** by Professor G. E. Coates, M.A. Joint Meeting with Oxford University Alembic Club to be held in the Physical Chemistry Laboratory, South Parks Road, Oxford.

ST. ANDREWS AND DUNDEE.

Thursday, November 1st, 1956, at 5.15 p.m.

Lecture by Professor Wilson Baker, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Friday, November 9th, 1956, at 5.15 p.m.

Lecture, **Application of Modern Techniques to Problems in Brewing,** by Professor I. A. Preece. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

SHEFFIELD.

Thursday, November 15th, 1956, at 7.30 p.m.

Lecture, **Chemotherapeutic Research,** by Dr. F. L. Rose, O.B.E., D.Sc., Ph.D., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and Sheffield University Chemical Society, to be held in the Chemistry Lecture Theatre, The University.

SOUTHAMPTON.

Friday, November 2nd, 1956, at 5 p.m.

Lecture, **Some Applications of Radiochemistry,** by Dr. R. Spence, C.B., F.R.I.C. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, The University.

Friday, November 23rd, 1956, at 5 p.m.

Lecture, **Some Aspects of the Organic Chemistry of Phosphorus,** by Professor H. N. Rydon, D.Sc., Ph.D., A.R.C.S., F.R.I.C. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, The University.

SOUTH WALES.

Monday, November 12th, 1956, at 5.30 p.m.

Lecture, **Some Radical Reactions,** by Dr. R. N. Haszeldine, M.A., Ph.D., F.R.I.C. To be given in the Chemistry Department, University College, Cardiff.

Friday, November 16th, 1956, at 6 p.m.

Lecture, **Some Recent Developments in Inorganic Stereochemistry,** by Professor R. S. Nyholm, D.Sc., Ph.D., F.R.I.C. Joint Meeting with the University College of Swansea Chemical Society to be held in the Chemistry Department, University College, Swansea.

Friday, November 23rd, 1956, at 6 p.m.

Lecture, **Factors Involved in the Production of Carbonium Ions,** by Professor A. G. Evans, D.Sc., Ph.D., F.R.I.C. Joint Meeting with the University College of Swansea Chemical Society to be held in the Chemistry Department, University College, Swansea.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Ernest Alexander Braude (Kew) (C. 1954—)	Jan. 22nd, 1942.	July 23rd, 1956.
Herbert Levinstein (Bletchley)	Dec. 3rd, 1914.	Aug. 3rd, 1956.
Neville Smith (Pontefract)	Sept. 15th, 1943.	June 4th, 1956.
Vivian John Weston (Ibadan)	Feb. 15th, 1945.	Apr. 7th, 1956.

ELECTION OF NEW FELLOWS.

The following 30 candidates were elected Fellows of the Society on August 13th, 1956:

Herbert I. Berman.
John Bull.
Thomas Ronald Capel.
Colin Gerald Coe.
Maria Di Fonzo.
Hans Feilchenfeld.
James Keith Hambling.
Thomas Andrew Hamor.
Puthupparambil Ittyerah Ittyerah.
John Bryan Jones.
Vlassios Krentos.
Carl Edward Lorenz.
Charles John Mandleberg.
Alton Meister.
Antonio Moriondo.
Norman Albert Perkins.
George Bouet Petersen.
Robert Peter Campbell Pockley.
Cyril Solomons.
Leslie Howard Sutcliffe.
Margaret Louise Swindells.
William John Thomas.
David Frank Tooley.
K. C. Tsou.
Brian Thomas Waters.
Alfred John Weinheimer.
David Willner.
Philip Daryl Wilmot.
John Allan Yates.
Martin John Zissell.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in November next. All persons who have received grants and whose accounts have not been declared closed by the Council are informed that reports must be received by the Society not later than November 1st, 1956.

Applications for grants, to be made on forms available from the General Secretary, must be received on or before November 15th, 1956. Applications from Fellows will receive prior consideration.

THE HARRISON MEMORIAL PRIZE

In accordance with the Trust Deed governing the Harrison Memorial Fund, the Selection Committee, consisting of the Presidents of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the Pharmaceutical Society, will, after December 1st, 1956, consider making an award of the Harrison Memorial Prize.

The Prize, not exceeding 100 Guineas, will be awarded to the chemist of either sex, being a natural-born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, shall, during the previous five years, have conducted the most meritorious and promising original investigations in chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should give the name of the applicant (in full), age (birth certificate should accompany the application), degrees (with name of University), any other qualifications and experience, titles of published papers (with co-authors' names), including full references to publication, where research was carried out, testimonials and references, and any other particulars bearing on the application.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates eligible for the Prize. Any such communication must be received by the President, The Chemical Society, Burlington House, Piccadilly, London, W.1, not

later that Saturday, December 1st, 1956. Candidates must not have attained the age of thirty years at this date.

CORDAY-MORGAN MEDAL AND PRIZE.

This award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 are due before the end of 1957.

ACKNOWLEDGMENTS.

The thanks of the Society have been conveyed to Dr. A. E. Parkes for a gift of publications.

75th ANNIVERSARY OF THE SOCIETY OF CHEMICAL INDUSTRY.

The President and Professor F. Bergel (Honorary Secretary) represented the Society at the Seventy-Fifth Anniversary Celebrations of the Society of Chemical Industry in July when the following address was presented :

THE CHEMICAL SOCIETY

TO THE

PRESIDENT, COUNCIL, AND MEMBERS

OF THE

SOCIETY OF CHEMICAL INDUSTRY

We, the President, Council, and Fellows of the Chemical Society, send you our greetings and felicitations on the occasion of the celebration of the seventy-fifth anniversary of the foundation of the Society of Chemical Industry.

On April 4th, 1881, at a meeting held in the Rooms of The Chemical Society in Burlington House, the inaugural meeting of the Society of Chemical Industry was held under the Chairmanship of Professor Sir Henry Roscoe, who was later elected your first President. Professor Roscoe, who held office as President of The Chemical Society from 1880 to 1882, referred in his Presidential Address of 1882 to the foundation of our Sister Society as " a matter for congratulation," and added, " The two Societies will, it is to be hoped, prove of mutual advantage." The history of the past seventy-five years shows how amply these hopes have been fulfilled, and it is our great pleasure to repeat them to-day.

It is our sincere wish that the Society of Chemical Industry, which this year comes into possession of fine premises of its own, may continue to play a leading part in the development of the many applications of fundamental chemical science, and may thus contribute in ever-increasing measure, to the advancement of knowledge and to the well-being and prosperity of mankind.

Signed on behalf of The Chemical Society,

E. L. Hirst
President.

Michael W. Perrin
Treasurer.

L. E. Sutton

F. Bergel

J. Chatt
Honorary Secretaries.

London, July 1956.

XVIth INTERNATIONAL CONGRESS FOR PURE AND APPLIED CHEMISTRY.

The XVIth International Congress for Pure and Applied Chemistry will take place in Paris from July 18th to 24th, 1957, simultaneously with the XIXth Conference of the International Union of Pure and Applied Chemistry. It will be preceded by the Centenary Celebrations of the Société Chimique de France.

The Congress will be divided into three Sections, for Physical, Inorganic, and Organic Chemistry.

Papers intended for the various Sections should deal with one of the following subjects :

In Physical Chemistry.

Physicochemical aspects of radioactive elements.
Combustion of gaseous mixtures.
Water in chemical compounds.
Diffusion in liquids and gels : reactions and structures.

In Inorganic Chemistry.

The solid compounds of transition metal (except complex compounds).
The compounds of boron with hydrogen and non-metallic elements.
Chemical properties of the elements in actinium series.
Chemical properties of substances at high temperature.

In Organic Chemistry.

Reaction mechanisms and intramolecular rearrangements.
Organometallic and organometalloidic compounds.
Selective reactions and orientation phenomena ; stereochemistry.
Structure and synthesis of natural compounds (except macromolecular substances).

Further details will be published in a later issue of *Proceedings*.

LIST OF APPLICATIONS FOR FELLOWSHIP

(*Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the* Journal *for September, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.*)

Ahmed, Khalil, M.Sc. (Punjab). Pakistani. 6, Sultan Teepu Street, Misri Shah, Lahore, West Pakistan. Research Fellow at the West Regional Laboratories, Lahore. *Signed by :* M. Hashmi, M. I. D. Chughtai.

Anderson, Douglas MacDonald Watt, B.Sc. and Ph.D. (Edin.), A.R.I.C. British. Department of Chemistry, The University, West Mains Road, Edinburgh, 9. Lecturer. *Signed by :* E. L. Hirst, G. O. Aspinall.

Barker, Leslie Oliver. British. Royal Hospital School, Nr. Ipswich, Suffolk. Science Master. *Signed by :* F. C. Lloyd, C. L. Geall.

Bayer, Raymond Philip, B.A. (Minnesota). American. Department of Chemistry, University of North Dakota, Grand Forks, North Dakota, U.S.A. Graduate Student. *Signed by :* V. H. Tiensuu, S. Pomerantz.

Bayer, Robert William, B.A. (Minnesota). American. Department of Chemistry, University of North Dakota, Grand Forks, North Dakota, U.S.A. Graduate Student. *Signed by :* V. H. Tiensuu, S. Pomerantz.

Becker, Robert R., M.S. and Ph.D. (Wisconsin). American. Department of Chemistry, Columbia University, New York 27, N.Y., U.S.A. Assistant Professor. *Signed by :* D. Kirschenbaum, G. Stork.

Corrodi, Hans Rudolph, D.Sc. and Dip.-Ing. Chem. (Zurich). Swiss. Schulhausstr. 34, Meilen, Switzerland. Research Assistant at ETH, Zurich. *Signed by :* V. Prelog, B. G. Engel.

Gream, George Edward, B.Sc. (New England). Australian. University of New England, Armidale, New South Wales, Australia. Student. *Signed by :* N. V. Riggs, J. E. Banfield.

Heaps, Eileen Violet. British. 14, Brockenhurst Gardens, Mill Hill, N.W.7. Undergraduate at Oxford University. *Signed by :* L. A. K. Staveley, R. E. Richards.

Hull, William Q., B.E. (Vanderbilt). American. American Chemical Society, Bush House, Aldwych W.C.2. European Editor. *Signed by:* E. K. Rideal, L. H. Lampitt.

Johnstone, Robert Alexander Walker, B.Sc. and Ph.D. (Sheffield). British. 30, Rutland Avenue, Sandal, Wakefield, Yorks. Research Student. *Signed by:* H. J. V. Tyrrell, T. S. Stevens.

Kreling, Maria Elisabeth. German. 4722, Maplewood Avenue, Montreal, P.Q., Canada. Research Chemist with Monsanto Canada, Ltd. *Signed by:* E. J. Tarlton, D. J. Whittingham.

Little, John Clayton, B.S. (California). American. 219, Noyes Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois, U.S.A. Graduate Student. *Signed by:* N. J. Leonard, D. Y. Curtin.

McKean, Donald Campbell, M.A. and D.Phil. (Oxon.). British. Chemistry Department, The University, Old Aberdeen. Lecturer. *Signed by:* R. H. Thomson, K. W. Bentley.

Merler, Ezio, B.A. and M.Sc. (British Columbia). Canadian. 17, Garrett Street, Kingston, Ontario, Canada. Student. *Signed by:* J. K. N. Jones, K. E. Russell.

Meyer, Hanan, Ph.D. (Jerusalem). Israeli. Department of Biological and Colloidal Chemistry, The Hebrew University, Jerusalem, Israel. Instructor in Biochemistry. *Signed by:* A. Neuberger, J. J. Scott.

Monks, Edward Robert, B.Sc. (Lond.). British. 52, Standen Avenue, Hornchurch, Essex. Research Student. *Signed by:* C. M. French, M. F. Ansell.

Murray, Robert Douglas Hutton. British. 33, Ayr Road, Prestwick, Ayrshire. Undergraduate at Glasgow University. *Signed by:* D. S. Payne, J. C. D. Brand.

Ohta, Tatsuo, D.Pharm. (Tokyo). Japanese. Tokyo College of Pharmacy, 600 Kashiwagi 2-Chome, Shinjuku-ku, Tokyo, Japan. Professor of Bacteriology and Phytochemistry. *Signed by:* S. Shibata, S. Sugasawa.

Seese, William S., B.S. (New Mexico). American. 8012, Morrow Road, N.E., Albuquerque, New Mexico. Research Assistant in Chemistry. *Signed by:* R. N. Castle, J. L. Riebsomer.

Slater, Arthur Walter, M.Sc. (Lond.). British. Flat 3, 14, Pembridge Crescent, London, W.11. Lecturer. *Signed by:* E. Boyland, F. Bergel.

Spotswood, Thomas McLeod, M.Sc. (Tasmania). British. 8, Browning Street, Clearview, Adelaide, South Australia. Research Chemist. *Signed by:* P. E. Rogasch, C. L. Cook.

Taylor, Sheila Ann. British. Imperial College Hostel, Prince Consort Road, South Kensington, S.W.7. Student. *Signed by:* J. Elvidge, D. M. Wells.

Thomas, Ann Margaret, B.S. (Pennsylvania). American. Chemistry Department, Indiana University, Bloomington, Indiana. Graduate Student. *Signed by:* V. J. Shiner, jun., F. Vratny.

Werbel, Leslie M., B.S. (Queens Coll.), M.A. (Columbia). American. 1208, W. California Street, Apartment 5, Urbana, Illinois, U.S.A. Graduate Student at Illinois University. *Signed by:* D. Y. Curtin, R. Adams.

Whitcutt, John Michael, B.Sc. (Rand.). South African. c/o National Chemical Research Laboratory, P.O. Box 395, Pretoria, South Africa. Research Chemist. *Signed by:* C. F. Garbers, J. P. de Villiers.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Bailey, William Charles, jun., B.S. (The Citadel). American. Chemistry Department, Emory University, Georgia, U.S.A. Student. *Signed by:* L. Mandell.

Eggers, Heinrich, Dr.rer.nat. (Gottingen). Rottmannstr. 29, Heidelberg, Germany. Student. *Signed by:* A. M. Meston.

Knowles, DeWitt C., jun., B.S. (Brooklyn Polytech.), M.S. (New York). American. Harris Research Laboratories, 1246, Taylor Street, N.W., Washington 11, D.C., U.S.A. Research Associate. *Signed by:* R. Saxon.

Pollack, Morris, M.S. (Brooklyn Polytech.), Ph.D. (Purdue). American. 2005, Vyse Avenue, New York 60, N.Y., U.S.A. Senior Research Chemist, Columbia-Southern Chemical Corp., Barbeuton. *Signed by:* G. Klee.

Sher, Murray Joel, B.S. (Boston Coll.), Ph.D. (New York). American. 734, Third Street, New Martinsville, West Virginia, U.S.A. Chemist with Columbia-Southern Chemical Corp. *Signed by:* J. W. Hellman.

Whitney, Ellsworth Dow, B.A. (Buffalo), Ph.D. (New York). American. 110, Alberta Drive, Eggertsville 21, New York, U.S.A. Research Chemist, Olin Mathieson Chemical Corp., Niagara Falls, New York. *Signed by:* R. J. F. Palchak.

Wilde, Richard Edward, jun., B.S. (California). American. 4213½, University Way, Apt. L., Seattle 5, Washington, U.S.A. Graduate Student at Washington University. *Signed by:* R. G. Neville.

PAPERS ACCEPTED

(List of Papers accepted between August 4th and August 27th, 1956, for publication in the *Journal*.)

" Thermal decomposition of mercuric *o*- and *m*-nitrobenzoates and 4-nitrophthalate." By P. S. MAYURANATHAN.

" Thermal decomposition of the mercuric and silver salts of the isomeric methyl hydrogen 3-nitrophthalates." By P. S. MAYURANATHAN.

" Crystal symmetry, and the adsorption of dyes by growing crystals. Part I. Ammonium nitrate IV." By JOHN WHETSTONE.

" Radical-capture agents in tetralin. Part I. Measurement of relative efficiencies and correlation with structure." By D. S. DAVIES, H. L. GOLDSMITH, A. K. GUPTA, and G. R. LESTER.

" Electronic spectra of organic molecules and their interpretation. Part II. Effect of terminal halogen atoms of conjugated systems on *K*-bands." By A. BURAWOY and A. R. THOMPSON.

" Some cholesteryl phosphates." By H. A. C. MONTGOMERY, J. H. TURNBULL, and W. WILSON.

" Synthesis of a dihydrosantonin isomer." By J. K. CHAKRABARTI, P. DUTT, and P. C. DUTTA.

" The reaction between aromatic compounds and derivatives of tertiary acids. Part VIII. The use of an infrared gas analyser for the quantitative determination of carbon monoxide." By MICHAEL E. GRUNDY, EUGENE ROTHSTEIN, and (in part) WEI-HWA HSÜ.

" The reaction between aromatic compounds and derivatives of tertiary acids. Part IX. Concentration and environmental factors influencing the elimination of carbon monoxide from pivaloyl chloride." By MICHAEL E. GRUNDY, EUGENE ROTHSTEIN, and (in part) WEI-HWA HSÜ.

" The identity of the cubic oxide present in films on iron." By D. EUROF DAVIES and U. R. EVANS.

" The structure of molecules and ions of the type $X_2A{\cdot}AX_2$, $X_2A{\cdot}AY_2$, and $YXA{\cdot}AXY$." By P. J. WHEATLEY.

" The thermodynamics of the formation of complex ions of ethylenediaminetetra-acetic acid and bivalent cations." By R. A. CARE and L. A. K. STAVELEY.

" Phenanthridines. Part I. The synthesis of bromophenanthridines." By G. M. BADGER and W. F. H. SASSE.

" Reduced cyclic compounds. Part II. The synthesis of 1-1'-acetoxyvinylcyclohexene and its reactions with some dienophils." By M. F. ANSELL and G. T. BROOKS.

" The relation between configuration and conjugation in diphenyl derivatives. Part VII. Halogenodiphenyls." By G. H. BEAVEN and D. MURIEL HALL.

" The composition of *Hakea acicularis* gum." By A. M. STEPHEN.

" Some 5α : 6α-epoxy-3-oxo-steroids." By BERNARD ELLIS and VLADIMIR PETROW.

" 4 : 4-Dimethyl-steroids. Part II. Some androstane and pregnane derivatives." By (MRS.) W. J. ADAMS, D. K. PATEL, V. PETROW, (MRS.) I. A. STUART-WEBB, and B. STURGEON.

" The polarography of some simple pyrazine derivatives." By L. F. WIGGINS and W. S. WISE.

" Phosphonic polymers. Part I. The copolymerisation of diethyl vinylphosphonate and styrene." By C. L. ARCUS and R. J. S. MATTHEWS.

" Several quinoxalines of biological interest." By R. M. ACHESON.

" Energy levels and absorption of some monosubstituted benzene derivatives." By A. MANGINI and C. ZAULI.

" The reaction between phosphorus trichloride and bromine." By G. S. HARRIS and D. S. PAYNE.

" Infrared spectra of metal ammines and related compounds. Part II. The *trans*-effect in platinous complexes." By D. B. POWELL.

"Spectra of transition metal complexes of the type $[Co(NH_3)_5X]^{++}$." By J. S. GRIFFITH and L. E. ORGEL.

"Carbamoylglyoxaline." By J. M. LOWENSTEIN.

"The reaction of tetra-alkylammonium halides with potassium in liquid ammonia." By D. A. HAZLEHURST, A. K. HOLLIDAY, and G. PASS.

"Aromatic reactivity. Part I. Effects of substituents on the removal of the trimethylsilyl group." By C. EABORN.

"Steroids and Walden inversion. Part XXXIV. The mechanism of deamination." By C. W. SHOPPEE, D. E. EVANS, and G. H. R. SUMMERS.

"Synthetical experiments in the chelidonine–sanguinarine group of alkaloids. Part IV." By A. S. BAILEY and C. R. WORTHING.

"By-ways of synthesis of cortisone from hecogenin. Part I. 9-Dehydrohecogenin as intermediate in preparation of 11-oxygenated compounds (11-oxotigogenin and 3β-acetoxy-17α-hydroxy*allo*pregnane-11 : 20-dione)." By R. K. CALLOW and V. H. T. JAMES.

"By-ways of synthesis of cortisone from hecogenin. Part II. A route to 11-oxygenated compounds through 3β : 20β-diacetoxy-11-bromo*allo*pregnan-12-one. By R. K. CALLOW and V. H. T. JAMES.

"The reduction of carbon monoxide by lithium aluminium hydride." By J. F. MARTIN, A. J. NEALE, and H. S. TURNER.

"Non-aqueous solutions of phosphorus pentabromide." By G. S. HARRIS and D. S. PAYNE.

"The chemical synthesis of polysaccharides. Part I. Synthesis of gentiodextrine." By S. HAQ and W. J. WHELAN.

"Tryptamines, carbolines, and related compounds. Part II. A convenient synthesis of tryptamines and β-carbolines." By R. A. ABRAMOVITCH and D. SHAPIRO.

"Tryptamines, carbolines, and related compounds. Part III. Scope of the method of synthesis of tryptamines. 1-Methyl- and *NN'*-dimethyl-tryptamines." By R. A. ABRAMOVITCH.

"The chemistry of santonin. Part III. The stereochemistry of some reduction products of santonin." By WESLEY COCKER and T. B. H. MCMURRY.

"4-Benzoyldiphenylamine." By M. P. LIPPNER and MURIEL L. TOMLINSON.

"2 : 6-Dimethylacetophenone." By (the late) E. A. BRAUDE and R. L. ERSKINE.

"The chemical action of ultrasonic waves." By A. V. M. PARKE and DUNCAN TAYLOR.

"Synthesis of polycyclic compounds. Part VI. The preparation of 1 : 2 : 3 : 4-tetrahydro-6-methoxy-4-*iso*propyl-1-oxonaphthalene and related compounds." By J. C. BARDHAN and D. N. MUKHERJI.

"Hydroaromatic steroid hormones. Part V. Some D-homo-18 : 19-bisnorsteroids." By A. J. BIRCH and HERCHEL SMITH.

"Water-soluble complexes of niobium (columbium) and tantalum. Part I. Complexes with α-hydroxy-acids and ethanolamines." By FRED FAIRBROTHER and JOHN B. TAYLOR.

ADDITIONS TO THE LIBRARY

Reagent chemicals; American Chemical Society specifications, 1955. (American Chemical Society. Committee on Analytical Reagents.) American Chemical Society. 1955.

Beilsteins Handbuch der Organischen Chemie, edited by F. Richter. 4th edn. Vol. 29. Part 1. General-Formelregister für das Hauptwerk und die Ergänzungswerke I und II. C_1–C_{11}. Springer-Verlag. 1956. (Presented by the Editor.)

Annual review of plant physiology, edited by L. R. Blinks, L. Machlis, and J. G. Torrey. Vol. 7. Annual Reviews, Inc. 1956.

Process chemistry, edited by F. R. Bruce *et al.* Vol. 1. (Progress in Nuclear Energy. Series III.) Pergamon Press Ltd. 1956.

Industrial research, 1956—1957, edited by P. Dunsheath. Todd Publishing Group Ltd. 1956.

Organic chemistry, by L. F. Fieser and M. Fieser. 3rd edn. Reinhold Publ. Corp. 1956.

Gmelins Handbuch der Anorganischen Chemie. Zink. Ergänzungsband. Systemnummer 32. 8th edn. Verlag Chemie, GMBH. 1956.

Chemistry of high degradation processes, by N. Grassie. Butterworths Scientific Publ. 1956.

The metallurgy of zirconium, edited by B. Lustman and F. Kerze, jun. McGraw-Hill Book Co., Inc. 1955.

A symposium on inorganic nitrogen metabolism: function of metallo-flavoproteins, edited by W. D. McElroy and B. Glass. Sponsored by the McCollum-Pratt Institute of Johns Hopkins University. Johns Hopkins Press. 1956.

The renaissance of inorganic chemistry. An inaugural lecture delivered at University College London, March 1956, by R. S. Nyholm. University College. 1956. (Presented by the Author.)

Biographisch-literarisches Handwörterbuch der exakten Naturwissenschaften. Band VIIa. Teil 1: A–E. 4 Lieferung, by J. C. Poggendorff. Akademie-Verlag. 1956.

The application of the mass spectrometer to the analysis of organic compounds, by J. D. Waldron. (*Metropolitan-Vickers Gazette*, 1956, **27**, (444), p. 220—228.) Metropolitan-Vickers. 1956. (Presented by the Publishers.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING DECEMBER, 1956

LONDON.

Thursday, December 13th, 1956, at 7.30 p.m.

Tilden Lecture, **Physical Properties of High Polymers in Relation to their Chemical Structures,** by Professor G. Gee, M.Sc., Ph.D., F.R.S. To be given in the Lecture Theatre, The Royal Institution, Albemarle Street, London, W.1.

ABERDEEN.

Friday, December 7th, 1956, at 7.30 p.m.

Lecture, **Polarographic Studies in Physical and Analytical Chemistry,** by Dr. W. Furness, B.Sc. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at Marischal College.

BRISTOL.

Thursday, December 6th, 1956, at 7 p.m.

Lecture, **Corrosion Fatigue and Stress Corrosion,** by Mr. T. D. Weaver and Dr. K. R. Wilson, M.S. Joint Meeting with the Royal Institute of Chemistry, the Institute of Metals, and the Corrosion and Chemical Engineering Groups of the Society of Chemical Industry, to be held in the Chemistry Department, The University.

CAMBRIDGE.

Monday, December 3rd, 1956, at 8.30 p.m.

Lecture, **Acetylene and *cyclo*Butadiene Complexes of the Transition Metals,** by Dr. M. C. Whiting, B.Sc. To be given in the University Chemical Laboratory, Lensfield Road.

EDINBURGH.

Thursday, December 6th, 1956, at 7.30 p.m.

Lecture, **The Application of Disintegrators and Conveyer Heat Exchangers in the Chemical and Food Industries,** by Mr. T. S. Ling. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at the North British Station Hotel.

IRISH REPUBLIC.

Wednesday, December 5th, 1956, at 7.45 p.m.

Lecture, **Algal Photosynthetic Pigments,** by Dr. Colm O hEocha, M.Sc., M.I.C.I. To be given in the Chemistry Department, University College, Dublin.

MANCHESTER.

Friday, December 7th, at 6.30 p.m.

Lecture, **New Aspects of the Sequestration of Metals,** by Dr. R. L. Smith, B.Sc., A.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Lecture Theatre, The University.

Thursday, December 13th, 1956, at 6.30 p.m.

Lecture by Professor J. Baddiley, D.Sc., Ph.D. To be given in the Chemistry Lecture Theatre, The University.

NORTHERN IRELAND.

Tuesday, December 4th, 1956, at 7.45 p.m.

Lecture, **The Oxidation of Hydrocarbons and Aldehydes in Solution,** by Professor C. E. H. Bawn, C.B.E., Ph.D., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at The Queen's University, Belfast.

SOUTHAMPTON.

Thursday, December 6th, 1956, at 8 p.m.

Lecture, **Degradation of High Polymers,** by Dr. N. Grassie, A.R.I.C. Joint Meeting with the University Chemical Society, the Plastics Institute and the Royal Institute of Chemistry, to be held in the Chemistry Department, The University.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Edward John Honess (Southsea)	Dec. 7th, 1916.	Aug. 14th, 1956.
Harold Lewis (W.C.2)	Mar. 16th, 1944.	May 19th, 1956.
Wilfrid Gustav Polack (Birmingham)	Dec. 2nd, 1915.	June 19th, 1956.
Noel Douglas Ridsdale (Middlesbrough)	Dec. 7th, 1911.	July 17th, 1956.
George Elliott Shaw (Tonbridge)	May 16th, 1895.	Feb., 1956.
Allan Frederick Walden (Oxford)	May 4th, 1899.	Apr. 19th, 1956.
William Wilson (Dumfries)	May 18th, 1944.	July 1st, 1956.

ELECTION OF NEW FELLOWS.

The following 69 candidates were elected to the Fellowship on September 17th, 1956:

Michael Anbar.
Judah Arotsky.
Muhammed Ashraf.
Derek Charles Bishop.
David Andrew Blackadder.
Solly Blumenfeld.
Carl Lee Bumgardner.
Hung-Chen Chiang.
Benjamin Peter Dailey.
Paul William Darby.
Robert Joseph Dummel.
Adrienne Gertrud Adele Eisner.
Bozidar V. Eric.
Frederick Peter Evans.
Robert Davis Faulkner.
George Roy Fitch.
James Horace William Forsythe.
William Good.
Harry Michael Gordon.
George Gorin.
Samuel Thomas Griffiths.
Brian John Thomas Harper.
Frank Reid Harvey.
Michael Roland Hatfield.
David Oldham Hayward.
John Hickman.
Tohru Hino.
Nobumasa Hojo.
Jack Ian Hoppe.
Ronald Whiteley Jackson.
Stanley Roy Johns.
George Johnson.
Philip Douglas Lawley.
Thomas Richard Layzell.
David Herbert Leaback.
Reuben Leberman.
William Richard Bruce Leigh.
Leslie Harry Little.
John Francis Lovett.
Peter Albert Lowe.
William Robert McGregor.
Dennis Joseph McHugh.
Frederick Arthur Pomroy Maggs.
Samuel S. Markowitz.
Montague Miller.
Samuel Martin Nelson.
Julian Harold Newland.
Judith Madeleine Nosworthy.
George Andrew Olah.
Michael Allan Owen.
Kenneth George Pickup.
John Pritchard.
Jack Rosenbaum.
Jan Olof Sandstrom.
Brahama Datta Sharma.
Michael Smith.
Bernard Peter Stark.
Peter John Stoward.
Swarup Narain Tewari.
Orlin Dalton Trapp, jun.
James Robert Turvey.
David Selway Urch.
Emy Marcelline Elizabeth von Bertele.
Edel Wasserman.
Elizabeth Jessie Williamson.
Clyde DeClifford Willson.
Brijnandan Prasad Yadava.
John Si Chiu Yan.
Ernst Zerner.

ACKNOWLEDGMENTS.

The thanks of the Society have been conveyed to Mr. F. O. Isaac and Dr. R. J. Woods for gifts of the Society's publications.

PROCEEDINGS OF THE CHEMICAL SOCIETY, 1957.

Council has approved plans for a change in the style, format, and contents of the Society's *Proceedings*. From January, 1957, *Proceedings* will be considerably increased in size by the inclusion of additional material which it is hoped will add greatly to the interest and permanent value of the publication. The new *Proceedings* will be given

without extra charge to all Fellows who have paid the basic annual subscription, or who are Life Fellows, and to all non-Fellows subscribing to the *Journal*. In addition, non-Fellows may, if they wish, subscribe separately to *Proceedings*.

In its new form *Proceedings* will no longer be issued as an insert in the *Journal*, but it will have its own distinctive cover, and will be printed in a more modern format on a white paper, thicker in substance than the tinted paper at present used. It will include lectures and obituary notices, and the Report of Council, which now appear in the *Journal*. It will also contain occasional articles, anonymous or signed, and personal news items concerning distinguished Fellows and visitors from overseas, as well as other news items of general interest, and the official announcements which already appear. Reports of Scientific Meetings held by the Society will be included, as well as short scientific " communications " which are sufficiently urgent or important to qualify for the accelerated publication and the greatly increased circulation that *Proceedings* will offer by comparison with the *Journal*. Notes regarding the submission of " communications " are given below. It is also expected that *Proceedings* will include, in addition to the advertisements at present printed in the *Journal*, a section of classified small advertisements, including notices of appointments vacant.

Considerably less than half the total Fellowship now receives the *Journal*, and *Proceedings* is, therefore, the only regular link which the Society has with many of its Fellows. The Council hopes that the improvements which are now planned will be welcomed by Fellows and by non-Fellows alike, and that they will form an attraction to prospective Fellows, and also will help to retain the interest of those Fellows who no longer need to subscribe to the Society's *Journal*.

" COMMUNICATIONS " FOR PROCEEDINGS, 1957.

Starting in January, 1957, *Proceedings of the Chemical Society* will be open to " Communications " which deal with original work of immediate importance to a substantial body of chemists, and manuscripts can now be accepted for consideration. It is unlikely that manuscripts received after December 18th, 1956, will be included in the first issue.

Publication will be granted only to " Communications " which satisfy each of the three requirements, *i.e.*, urgency, importance, and wide interest. The primary consideration will be that chemists in general shall benefit from information in advance of full publication. The object shall be to share knowledge, not claim priority or reserve a field. Polemics, including prolonged argument about known experimental facts, would not be acceptable.

Details of experimental methods will not be published unless they are an essential part of the " Communications," nor will the physical or chemical properties of intermediates in syntheses or degradations.

" Communications " will be considered for publication whether or not the author is a Fellow of the Chemical Society. They will be subject to refereeing, and, if accepted, to editing. Authors are advised to submit, with the manuscript, a statement for the benefit of the referees setting out briefly the reasons why publication in advance of full presentation is requested.

Authors whose " Communications " are accepted should consider themselves under obligation to publish adequate details as soon as possible, or to withdraw the claims made, but not necessarily in a publication of the Chemical Society.

Manuscripts must be marked " Communication for Proceedings " and sent, in duplicate, to the Honorary Secretaries, The Chemical Society, Burlington House, Piccadilly, London, W.1. They should not normally exceed 600 words in length, *i.e.*, three quarto pages in double-line spacing, including formulæ or diagrams, which should be kept to a minimum and may delay publication. It is hoped that in the coming year accepted " Communications " will be published within four to eight weeks of receipt.

Authors should observe the Society's conventions for nomenclature, symbolism, etc., outlined in the brochure " The Presentation of Papers for the Journal of the Chemical Society," but references should be given as footnotes (see *Proceedings of the Chemical Society*, July 1955, pp. 79—81.)

THE HARRISON MEMORIAL PRIZE.

In accordance with the Trust Deed governing the Harrison Memorial Fund, the Selection Committee, consisting of the Presidents of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry, and the Pharmaceutical Society, will, after December 1st, 1956, consider making an award of the Harrison Memorial Prize.

The Prize, not exceeding 100 Guineas, will be awarded to the chemist of either sex, being a natural-born British subject and not at the time over thirty years of age, who, in the opinion of the Selection Committee, shall, during the previous five years, have conducted the most meritorious and promising original investigations in chemistry and published the results of those investigations in a scientific periodical or periodicals.

Applications, five copies of which must be submitted, should give the name of the applicant (in full), age (birth certificate should accompany the application), degrees (with name of university), any other qualifications and experience, titles of published papers (with co-authors' names), including full references to publications, where research was carried out, testimonials and references, and any other particulars bearing on the application.

The Selection Committee is prepared to consider applications, nominations, or information as to candidates eligible for the Prize. Any such communication must be received by the President, The Chemical Society, Burlington House, Piccadilly, London, W.1, not later than Saturday, December 1st, 1956. Candidates must not have attained the age of thirty years at this date.

CORDAY–MORGAN MEDAL AND PRIZE.

This award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 and due before the end of 1957.

THE CORDAY–MORGAN COMMONWEALTH FELLOWSHIP.

Applications are invited from citizens of any country within the British Commonwealth for The Corday–Morgan Commonwealth Fellowship. This will be awarded for post-doctorate (or equivalent) study in any branch of Chemistry. It will be tenable for one year in some part of the British Commonwealth other than that in which the candidate received his scientific education, at any university, research institution, or other place of study approved by the Corday–Morgan Memorial Fund Executive.

The value of the Fellowship will be £700 per annum, but additional allowances may be granted in appropriate cases for travel, university fees, etc. The appointment will date from October 1st, 1957, or such other date as may be arranged.

The appointment will be made by the Executive not later than May 10th, 1957.

Application forms and copies of the General Regulations governing the Award may be obtained from The Secretary, Corday–Morgan Memorial Fund Executive, c/o The Chemical Society, Burlington House, London, W.1.

Applications must be received by the Secretary not later than March 1st, 1957.

THE ROYAL INSTITUTE OF CHEMISTRY—THE MELDOLA MEDAL.

This medal is the gift of the Society of Maccabæans, and is normally awarded annually. The next award will be made early in 1957 to the chemist who, being a British subject and under 30 years of age at December 31st, 1956, shows the most promise, as indicated by his or her published chemical work brought to the notice of the Council of the Royal Institute of Chemistry before December 31st, 1956.

No restrictions are placed upon the kind of chemical work or the place in which it is

conducted. The merits of the work may be brought to the notice of the Council, either by persons who desire to recommend the candidate or by the candidate himself, by letter addressed to The President, The Royal Institute of Chemistry, 30 Russell Square, London, W.C.1, the envelope being marked " Meldola Medal."

The letter should be accompanied by six copies of a short statement on the candidate's career (date of birth, education and experience, degrees and other qualifications, special awards, etc., with dates) and of a list of titles, with references, of papers or other works published by the candidate, independently or jointly. Candidates are also advised to forward one reprint of each published paper of which copies are available.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objections to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the Journal *for October,* 1956. *Such objections will be treated as confidential. The forms of application are available in the Library.)*

Balon, Anthony Derek John, B.Pharm. (Lond.). British. 30, Sherwood Road, London, N.W.4. Research Student. *Signed by:* A. F. Casy, A. H. Beckett.

Batres, Enrique. Mexican. Syntex, S.A., Apdo. Postal 2679, Mexico, D.F., Mexico. Research Chemist. *Signed by:* O. Mancera, F. A. Kincl.

Beanland, Eric, B.Sc. (Lond.). British. 11, Chequers Lane, Walton-on-the-Hill, Tadworth, Surrey. Research Chemist. *Signed by:* A. G. Lidstone, A. J. Lindsey.

Berkoff, Charles Edward, B.Sc. (Lond.). British. 10, British Street, Bow, London, E.3. Research Fellow at Imperial College of Science & Technology. *Signed by:* H. T. Young, A. G. Cooper.

Brown, Barry Tebbutt, M.Sc. (Sydney). Australian. 200, Pacific Highway, Lindfield, N.S.W., Australia. University Lecturer. *Signed by:* T. R. Watson, S. E. Wright.

Cossey, Hugh Douglas, B.Sc. (Lond.). British. 19, Top Park, Beckenham, Kent. Research Student. *Signed by:* C. M. Atkinson, D. R. Goddard.

Cowell, David Brian, B.Pharm. and Ph.D. (Lond.), A.R.I.C. British. 10, Upton Villas, Upton Road, Bexleyheath, Kent. Lecturer at Chelsea Polytechnic. *Signed by:* A. F. Casy, A. H. Beckett.

Di Giorgio, Joseph Brun, B.E. (The Johns Hopkins Univ.). American. Department of Chemistry, The Johns Hopkins University, Baltimore 18, Maryland, U.S.A. Student. *Signed by:* A. Nickon, F. J. McGuire.

Groocock, John Michael, B.Sc. and Ph.D. (Lond.), D.I.C., A.R.C.S. British. 3, Dale Court, Homesdale Road, Bromley, Kent. Senior Scientific Officer with the Ministry of Supply. *Signed by:* P. J. F. Griffiths, F. C. Tompkins.

Grout, Raymond John, B.Pharm. (Notts.). British. 178, Cinderhill Road, Bulwell, Nottingham. Assistant Lecturer at Nottingham University. *Signed by:* T. J. King, F. C. Cooper.

Hall, Charles Dennis, B.Sc. (Lond.). British. 191, Charlestown Road, Blackley, Manchester, 9. Research Student at London University. *Signed by:* A. C. Farthing, R. G. A. New.

Maddern, Joseph Thomas. British. 17, Rectory Road, Stanley Green, Poole, Dorset. Power Station Chemist with Central Electricity Authority. *Signed by:* T. F. McCombie, G. D. Muir.

Morcom, Kenneth Wintle, B.Sc. (Reading). British. Coppid House, Rectory Road, Wokingham, Berks. Research Student at Reading University. *Signed by:* M. C. McGlashan, K. W. Allen.

Nishiwaki, Taro, B.Sc. (Tokyo). Japanese. c/o Tokaryo, 5981 Banchi, 4-Chome, Kamiitabashi, Itabashi-ku, Tokyo, Japan. Postgraduate Student at Tokyo University. *Signed by:* S. Yoshida, S. Tanaka.

Robinson, Arthur Graham. British. 21, Finchley Grove, Moston, Manchester, 10. Assistant Technical Manager. *Signed by:* E. A. Duligal, B. S. Jackson.

Seyferth, Dietmar, B.A. (Buffalo), M.A. and Ph.D. (Harvard). American. Department of Chemistry, Harvard University, 12, Oxford Street, Cambridge 38, Massachusetts, U.S.A. Research Fellow. *Signed by:* F. G. A. Stone, L. N. Mulay.

Smith, Audrey Taylor, B.Sc. (Lond.), A.R.C.S. British. 77, Wintworth Road, Banstead, Surrey. Postgraduate Research Fellow at St. Mary's Hospital Medical School, W.2. *Signed by:* A. Neuberger, J. J. Scott.

Swift, Douglas, B.Pharm. (Lond.). British. 136, Holland Road, London, W.14. Research Student. *Signed by:* A. H. Beckett, J. Walker.

Taylor, James Welch, B.A. (Vanderbilt). American. 1790, Brooks Road, Memphis, Tennessee, U.S.A. Graduate Student at Georgia Institute of Technology. *Signed by:* E. Grovenstein, jun., J. Hine.

Theobald, David William. British. The School House, Sandford-on-Thames, Oxford. Student at Oxford University. *Signed by:* J. C. Smith, M. L. Tomlinson.

Vaidyanathan, Chelakara Sivarama, M.Sc. and Ph.D. (Madras). Indian. Department of Botany, University College, Singleton Park, Swansea. Senior Research Fellow. *Signed by:* C. W. Shoppee, E. E. Ayling.

Wagner, Peter Frederick, B.Sc. (Lond.). British. 2, Fordwich Road, Welwyn Garden City, Herts. Assistant Analyst with Smith & Nephew Research Ltd., Ware. *Signed by:* F. J. Macrae, K. A. Kerridge.

PAPERS ACCEPTED

(List of Papers accepted between August 28th and September 17th, 1956, for publication in the *Journal*.)

"Adsorption from binary liquid mixtures on activated alumina." By J. J. KIPLING and D. B. PEAKALL.

"The infrared absorption spectra of the carbonyl group in methoxyanthraquinones, and in the hydrochlorides of α-methoxyanthraquinones." By L. A. WILES and L. C. THOMAS.

"Oxidation of organic compounds by solid manganese dioxide." By M. Z. BARAKAT, M. F. ABDEL WAHAB, and M. M. EL-SADR.

"Observations on ammonium ferric disulphate dodecahydrate (ammonium ferric alum) and some of its derivatives." By HENRY BASSETT.

"A polarographic study of copper malonate complexes." By E. GELLES and G. H. NANCOLLAS.

"Border-line mechanisms in nucleophilic displacement reactions." By V. GOLD.

"A new and specific aromatisation reaction. Part II. Some further examples." By P. A. ROBINS and JAMES WALKER.

"The polycondensation of benzyl chloride catalysed by stannic chloride." By L. VALENTINE and R. W. WINTER.

"Kinetics of the decarboxylation of oxaloacetic acid." By E. GELLES.

"Syntheses in the quinazolone series. Part V. Synthesis of 7-oxobenzo[*d*]quinazo-[3 : 2-*b*]thiazole 5 : 5-dioxide, and of 2-*o*-sulphamylphenyl-3*H*-quinazol-4-one." By EDITH STEPHEN and HENRY STEPHEN.

"The preparation of 2-acyl-3-oxo-4 : 5-benzo-1 : 2-thiazoline 1 : 1-dioxides (*N*-acyl-saccharins) for the identification of monocarboxylic acids." By EDITH STEPHEN and HENRY STEPHEN.

"Phosphorescence and fluorescence of some aromatic nitroamines." By R. FOSTER, D. LL. HAMMICK, G. M. HOOD, and A. C. E. SANDERS.

"The denitration of *N*-methyl-*N'*-nitroguanidine." By MURIEL L. HARDY.

"Infrared spectra of natural products. Part VII. The characterization of equatorial and axial 3-hydroxyl groups in triterpenoids." By (MISS) I. L. ALLSOP, A. R. H. COLE, D. E. WHITE, and R. L. S. WILLIX.

"The formation of osazones during attempted Fischer indole syntheses." By D. A. KINSLEY and (the late) S. G. P. PLANT.

"Organic peroxides. Part VII. The alkylation of hydrogen peroxide and alkyl hydroperoxides with ethers." By ALWYN G. DAVIES and R. FELD.

"Steroids and Walden inversion. Part XXXV. Solvolysis of cholesteryl toluene-*p*-sulphonate with thiophenoxide ions." By C. W. SHOPPEE, H. C. RICHARDS, and G. H. R. SUMMERS.

"Steroids and Walden inversion. Part XXXVI. *NN*-Dimethylcholest-7-en-3α-yl and -3β-ylamines." By D. E. EVANS and G. H. R. SUMMERS.

"Quassin and *neo*quassin. Part V." By R. J. S. BEER, B. G. DUTTON, D. B. JAQUISS, ALEXANDER ROBERTSON, and W. E. SAVIGE.

"Experiments on the preparation of indolocarbazoles. Part IX. The preparation of 9-methylindolo(2′ : 3′-1 : 2)carbazole." By R. J. BRUNTON, F. K. DRAYSON, (the late) S. G. P. PLANT, and MURIEL L. TOMLINSON.

"Quantitative microestimation of formaldehyde in the presence of periodate and its application to the structural examination of carbohydrate phenylosazones." By L. HOUGH, D. B. POWELL, and B. M. WOODS.

"Structure and reactivity of the oxy-anions of transition metals. Part II. Investigations by electron-spin resonance." By A. CARRINGTON, D. J. E. INGRAM, D. SCHONLAND, and M. C. R. SYMONS.

"Aryldihydroresorcinols. Part II. The influence of the nitro-group in dihydro-5-*o*-nitrostyrylresorcinol." By E. E. AYLING and D. A. DAVIES.

"Nucleotides. Part XXXIX. 5′-Deoxy-5′-iodo-O^2:2′-*cyclo*uridine: an *X*-ray crystallographic study." By D. M. BROWN, W. COCHRAN, E. H. MEDLIN, and S. VARADARAJAN.

"Electrophilic substitution. Part VIII. The nitration of dibenzofuran and a new method of ultraviolet spectrophotometric analysis of mixtures." By M. J. S. DEWAR and D. S. URCH.

"The action of tin and hydrochloric acid on *p*-dialkylaminobenzaldehydes. Part I. The mechanism of the reaction." By FREDERICK H. C. STEWART.

"Urinary steroids and related compounds. Part I. 11-Substituted derivatives of androsterone." By W. KLYNE and SHEILA RIDLEY.

ADDITIONS TO THE LIBRARY

Chemical engineering practice, edited by H. W. Cremer. Vol. I. General. Butterworths Scientific Publications, 1956. (Presented by the Editor.)

Chemical engineering practice, edited by H. W. Cremer. Vol. II. Solid State. Butterworths Scientific Publications, 1956. (Presented by the Editor.)

Organic chemistry, by I. L. Finar. Vol. 2. Stereochemistry and the chemistry of natural products. Longmans, Green & Co. 1956. (Presented by the Author.)

Handbuch der analytischen Chemie, edited by W. Fresenius and G. Jander. Vol. 2. Qualitative Nachweisverfahren. Part 4aB, Elemente der Vierten Hauptgruppe, II. Germanium; Zinn, edited by H. Haraldsen. Springer-Verlag. 1956.

Handbuch der analytischen Chemie, edited by W. Fresenius and G. Jander. Vol. 3. Quantitative Bestimmungs-und Trennungsmethoden. Part 3aB/3b, Elemente der dritten Hauptgruppe, II, und der dritten Nebengruppe. Gallium, Indium, etc.; edited by A. Brukl, *et al.* 2nd edn. Springer-Verlag. 1956.

Microrecording: industrial and library applications, by C. M. Lewis and W. H. Offenhauser, jun. Interscience Publishers, Inc. 1956.

Reports on progress in physics. Vol. 18, 1955. Physical Society. 1955.

Reports on progress in physics. Vol. 19, 1956. Physical Society. 1956.

Photosynthesis and related processes, by E. I. Rabinowitch. Vol. 2. Part 2. Interscience Publishers, Inc. 1956.

Chemistry of carbon compounds: a modern comprehensive treatise, edited by E. H. Rodd. Vol. 3. Part B. Aromatic compounds. Elsevier Publishing Co. 1956.

The Canadian Petrochemical Industry, by Shell Oil Co. of Canada, Ltd., Chemical Division. Ryerson Press. 1956. (Presented by Shell Petroleum Co., Ltd.)

Acta Metallurgica. 1953, Vol. 1, No. 1. (New periodical.) Pergamon Press, Inc., U.S.A.

Boletim do Departamento de Quimica. Universidade de Sao Paulo. Escola Politécnica. 1955. No. 1. (New periodical.) Universidade de Sao Paulo.

Proceedings of the Academy of Sciences of the U.S.S.R. Section: Agrochemistry. (Translation of section of *Doklady*). 1956, Vol. 106, No. 1. (New periodical.) Consultants Bureau, Inc., New York.

Proceedings of the Academy of Sciences of the U.S.S.R. Section: Geochemistry. (Translation of section of *Doklady*.) 1956, Vol. 106, No. 1. (New periodical.) Consultants Bureau, Inc., New York.

Revista de la Facultad de Quimica. Universidad Nacional Mayor de San Marcos. 1955, Vol. 7, No. 1. Universidad Nacional Mayor de San Marcos, "Editorial San Marcos," Lima, Peru.

Rubber and Plastics Age. 1956, Vol. 37, No. 8. Rubber and Technical Press, Ltd., London. (Presented by the Publishers.)

Science Reports of the Society for the Research of Theoretical Chemistry. Japan. 1955, Vol. 1, No. 1. (New periodical.) Society for the Research of Theoretical Chemistry, Kinki University, Osaka-fu, Japan. (Presented by the publishers.)

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING JANUARY, 1957

LONDON.

Thursday, January 17th, 1957, at 7.30 p.m.

The following papers will be presented :

"The Kinetics of the Rearrangement and Oxidation Reactions of Hydrazobenzene in Solution." By D. A. Blackadder.

"The Rôle of the Solvent, Catalyst, and Co-catalyst in the $SnCl_4$-catalysed Polymerisation of Styrene." By R. O. Colclough.

"The Decomposition of Lead Tetra-acetate in Acetic Acid." By L. H. Sutcliffe.

To be held in the Rooms of the Society, Burlington House, W.1. Abstracts of the papers may be obtained from the General Secretary.

BIRMINGHAM.

Friday, January 18th, 1957, at 4.30 p.m.

Lecture, **The Structure and Chemistry of the Living Cell,** by Dr. T. S. Work, B.Sc. Joint Meeting with Birmingham University Chemical Society to be held in the Chemistry Department, The University.

Friday, January 25th, 1957, at 4.30 p.m.

Lecture, **Some Recent Studies in Relation to Biosynthesis,** by Professor A. J. Birch, D.Phil. Joint Meeting with Birmingham University Chemical Society to be held in the Chemistry Department, The University.

BRISTOL.

Thursday, January 17th, 1957, at 7 p.m.

Lecture, **Some Aspects of Radiation Chemistry,** by Professor F. S. Dainton, M.A., Ph.D. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

CAMBRIDGE.

Monday, January 21st, 1957, at 8.30 p.m.

Lecture, **Radiation—Chemical Reactions in Aqueous and Non-aqueous Solutions,** by Dr. E. Collinson, M.A. To be given in the University Chemical Laboratory, Pembroke Street.

EDINBURGH.

Thursday, January 10th, 1957, at 7.30 p.m.

Lecture, **Chocolate Manufacture with Special Reference to Cacao Constituents,** by Mr. H. B. Brown. Joint Meeting with the Royal Institute of Chemistry, the Society of Chemical Industry, and the Food Group of the Society of Chemical Industry, to be held at the North British Station Hotel.

LEEDS.

Monday, January 14th, 1957, at 6.30 p.m.

Royal Institute of Chemistry Lecture, **Problems of Air Pollution,** by Mr. G. Nonhebel, B.A., B.Sc., F.R.I.C. To be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

Monday, January 21st, 1957, at 7.0 p.m.

Society of Chemical Industry Lecture, **Fibre Science and Leather Production,** by Dr. H. Phillips, F.R.I.C. To be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

MANCHESTER.

Wednesday, January 16th, 1957, at 6.30 p.m.

Lecture, **Studies of Knock and Anti-knock by Kinetic Spectroscopy,** by Professor R. G. W. Norrish, Sc.D., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Lecture Theatre, The University.

NEWCASTLE AND DURHAM

Friday, January 25th, 1957, at 5.30 p.m.

Bedson Club Lecture, **Polymerisation in Heterogeneous Systems,** by Professor C. E. H. Bawn, Ph.D., F.R.S. To be given in Chemistry Building, King's College, Newcastle upon Tyne, 1. (All Fellows are invited.)

NORTHERN IRELAND.

Tuesday, January 28th, 1957, at 7.15 p.m.

Lecture, **Paint Research—Electron Microscopy and Related Techniques,** by Mr. T. R. Bullett, B.Sc., A.Inst.P. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at The Queen's University, Belfast.

NOTTINGHAM AND LEICESTER.

Monday, January 21st, 1957, at 4.30 p.m.

Lecture, **Some Recent Developments in Free-radical Chemistry,** by Professor D. H. Hey, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the Chemical Society of the University College of Leicester to be held at University College, Leicester.

Tuesday, January 22nd, 1957, at 4.45 p.m.

Lecture, **Old Metals and New Valencies,** by Professor R. S. Nyholm, D.Sc., Ph.D., F.R.I.C. Joint Meeting with Nottingham University Chemical Society to be held in the Lecture Theatre, Chemistry Department, The University, Nottingham.

SHEFFIELD.

Thursday, January 17th, 1957, at 7.30 p.m.

Lecture, **Modern Inorganic Stereochemistry,** by Professor R. S. Nyholm, Ph.D., D.Sc., F.R.I.C. Joint Meeting with Sheffield University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

SOUTHAMPTON.

Friday, January 18th, 1957, at 5.0 p.m.

Lecture, **Structure Action Relationships of Hypotensive Drugs,** by Dr. H. R. Ing, F.R.S. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, The University.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
Clarence Pridmore Andrew (Johannesburg)	May 6th, 1920.	Aug. 26th, 1956.
Robert William Kinkead (Lisburn)	May 5th, 1921.	July 25th, 1956.
John Beresford Leathes (Oxford)	June 21st, 1900.	Sept. 14th, 1956.
Richard May (London, W.5)	June 15th, 1889.	Aug. 23rd, 1955.
Vallilyil Govindan Nair (Malabar)	Dec. 1st, 1910.	April, 1956.
Isaac Stern (London, S.E.11)	Sept. 17th, 1942.	Aug. 1st, 1956.

The Council also regrets to announce the death on October 8th of Mr. A. E. Cummins, former Librarian. An obituary notice will be published.

ELECTION OF NEW FELLOWS.

The following 33 candidates were elected to the Fellowship on October 18th, 1956:

Khalil Ahmed.
Douglas MacDonald Watt Anderson.
William Charles Bailey, jun.
Leslie Oliver Barker.
Raymond Philip Bayer.
Robert William Bayer.
Robert R. Becker.
Hans Rudolph Corrodi.
Heinrich Eggers.
George Edward Gream.
Eileen Violet Heaps.
William O. Hull.
Robert Alexander Walker Johnstone.
DeWitt C. Knowles, jun.
Maria Elisabeth Kreling.
John Clayton Little.
Donald Campbell McKean.
Ezio Merler.
Hanan Meyer.
Edward Robert Monks.
Robert Douglas Hutton Murray.
Tatsuo Ohta.
Morris Pollack.
William S. Seese.
Murray Joel Sher.
Arthur Walter Slater.
Thomas McLeod Spotswood.
Sheila Ann Taylor.
Ann Margaret Thomas.
Leslie M. Werbel.
John Michael Whitcutt.
Ellsworth Dow Whitney.
Richard Edward Wilde, jun.

CORDAY-MORGAN MEDAL AND PRIZE.

This award, consisting of a Silver Medal and a monetary Prize of 200 Guineas, is made annually to the chemist of either sex and of British Nationality who, in the judgment of the Council of the Chemical Society, has published, during the year in question, the most meritorious contribution to experimental chemistry, and who has not, at the date of publication, attained the age of thirty-six years.

Copies of the rules governing the Award may be obtained from the General Secretary of the Society. Applications or recommendations in respect of the Award for the year 1955 must be received not later than December 31st, 1956, and applications for the Award for 1956 are due before the end of 1957.

LIBRARY.

The Library will be closed from 1 p.m., Saturday, December 22nd, until 10 a.m., Friday, December 28th, 1956.

AMERICAN CHEMICAL SOCIETY PUBLICATIONS 1957.

The non-member prices of American Chemical Society publications for 1957 are given in the Table. The domestic subscription rates given in the table apply to subscribers in the United States and Canada only.

Under a reciprocal agreement Fellows of the Chemical Society may enter subscriptions to the journals published by the American Chemical Society at a discount of 10 per cent.

from the non-members' rates. This discount does not apply to *Chemical Abstracts*, which is no longer published as a periodical but is authorised and priced as a service.

All enquiries should be addressed to The American Chemical Society, 1155 Sixteenth Street, N.W., Washington, 6, D.C., U.S.A.

Title	Subscription classification	Subscription rates 1 year	2 years	3 years	Postage extra, yearly Foreign.	Canadian.
Chemical Abstracts Service with Indexes	Colleges and Universities * (Foreign or Domestic)	$80.00	None	None	$3.00	$1.00
	All Others (Foreign or Domestic)	350,00	,,	,,	None	None
Chemical Abstracts Service without Indexes	Colleges and Universities * (Foreign or Domestic)	65.00	,,	,,	2.40	0.80
	All Others (Foreign or Domestic)	320.00	,,	,,	None	None
Industrial and Engineering Chemistry	Domestic and Canadian	5.00	$8.00	$11.00	—	0.90
	Foreign except Canada	15.00	27.50	40.00	2.70	—
Chemical and Engineering News	Domestic (ditto)	6.00	10.00	14.00	—	1.00
	Foreign (ditto)	15.00	27.50	40.00	3.00	—
Journal of Agricultural and Food Chemistry	Domestic (ditto)	6.00	11.00	15.00	—	0.50
	Foreign (ditto)	12.00	22.00	30.00	1.50	—
Analytical Chemistry	Domestic (ditto)	5.00	9.00	12.00	—	0.50
	Foreign (ditto)	15.00	27.50	40.00	1.50	—
Journal of the American Chemical Society	Domestic (ditto)	30.00	None	None	—	1.10
	Foreign (ditto)	30.00	,,	,,	3.30	—
The Journal of Physical Chemistry	Domestic (ditto)	16.00	,,	,,	—	0.40
	Foreign (ditto)	16.00	,,	,,	1.20	—
The Journal of Organic Chemistry	Domestic (ditto)	25.00	,,	,,	—	0.50
	Foreign (ditto)	25.00	,,	,,	1.50	—

* Teaching institutions are required to sign a certificate that the teaching or training of students is their principal object.

All American Chemical Society journals and services are available to its Members at special prices which are available on request. No discount is given on Member subscriptions.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held at Burlington House on Thursday, October 18th, 1956, at 7.30 p.m.

The President, PROFESSOR E. L. HIRST, M.A., D.Sc., F.R.S., was in the Chair.

MINUTES.

The Minutes of the Scientific Meetings held at Burlington House on June 7th and at the University College of North Staffordshire, Keele, from July 16th to 19th, circulated in the *Proceedings* for July and August, respectively, were taken as read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: R. J. W. Cremlyn, T. R. Layzell, Douglas W. Russell, J. J. Lawler, S. S. Brown.

SCIENTIFIC COMMUNICATIONS.

The following papers were presented:

"Hydroaromatic Steroid Hormones. Part V. Some D-Homo-18: 19-bisnorsteroids." By A. J. Birch and Herchel Smith.

"The Reduction of Diphosphopyridine Nucleotide and Some Model Compounds by means of *X*-Rays." By G. Stein and A. J. Swallow.

" By-ways of Synthesis of Cortisone from Hecogenin. Part I. 9-Dehydrohecogenin as Intermediate in the Preparation of 11-Oxygenated Compounds (11-Oxotigogenin and 3β-Acetoxy-5α-pregnan-17α-ol-11 : 20-dione). Part II. A Route to 11-Oxygenated Compounds through 11-Bromo-5α-pregnane-3β : 20β-diol-12-one Diacetate." By R. K. Callow and V. H. T. James.

Minutes of a

SCIENTIFIC MEETING

held in the College of Technology, Manchester, on Friday, October 19th, 1956, at 6.30 p.m.

The President, PROFESSOR E. L. HIRST, M.A., D.Sc., F.R.S., was in the Chair.

Professor H. N. Rydon welcomed the Society to the College of Technology, Manchester, and the President replied.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: G. D. Meakins, H. L. Roberts, W. W. Jones.

LECTURE.

The President called upon Dr. S. C. Abrahams to deliver a lecture entitled " Recent Studies in the Stereochemistry of Sub-group VIB." At the conclusion of the Lecture a vote of thanks to Dr. Abrahams, proposed by Dr. F. Fairbrother, was carried with acclamation.

LIST OF APPLICATIONS FOR FELLOWSHIP

(*Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the* Journal *for November*, 1956. *Such objections will be treated as confidential. The forms of application are available in the Library.*)

Alderson, Geoffrey Winton, B.A. (Cantab.). British. Gonville and Caius College, Cambridge. Research Student. *Signed by:* G. W. Kenner, V. M. Clark.

Ardon, Michael, M.Sc. (Jerusalem). Israeli. Batei Biberman, Block II, Jerusalem, Israel. Senior Assistant at The Hebrew University, Jerusalem. *Signed by:* E. A. Halevi, H. J. G. Hayman.

Asolkar, Gopal Vishvanath, M.Sc. and Ph.D. (Nagpur). Indian. University Chemical Laboratory, Lensfield Road, Cambridge. Research Student. *Signed by:* H. J. Emeléus, R. N. Haszeldine.

Ashworth, John, M.Sc.Tech. (Manc.), A.M.T.C. British. 29, Malvern Avenue, Preston. Head of Textiles Department, Harris Institute Technical College, Preston. *Signed by:* L. A. Whalley, H. Brown.

Baker, James Albert, B.Sc. and Ph.D. (Lond.), A.R.I.C. British. 92, Farm Hill, Woodingdean, Brighton 7. Senior Lecturer in Pharmaceutical Chemistry. *Signed by:* A. R. Rogers, J. S. Coe.

Bean, Peter John, B.Sc. (Bris.). British. 50, Catherine Street, Salisbury, Wilts. Student at Bristol University. *Signed by:* A. C. M. Finch, P. Woodward.

Behr, Omri Marc Nathan, B.A. (Oxon.). British. 2, Telegraph Hill, Platts Lane, London, N.W.3. Research Student. *Signed by:* R. E. Richards, T. G. Halsall.

Betts, Brian Ernest, B.Sc. (Lond.). British. St. Edmunds, Cruthavon Rise, Witham, Essex. Research Student. *Signed by:* G. R. Ames, W. Davey.

Blackburn, George Michael, B.A. (Cantab.). British. Chemistry Department, The University, Nottingham. Post-graduate Student. *Signed by:* R. J. Martin, G. Read.

Burrell, John William Kidman, B.Sc. (Lond.), A.R.C.S. British. 164, Widmore Road, Bromley, Kent. Research Student at Imperial College. *Signed by:* L. Crombie, J. A. Elvidge.

Chapman, Frederick Brian, B.Sc. (Lond.), A.R.C.S. British. Standeven House, Broomfield Avenue, Halifax. Postgraduate Research at Imperial College. *Signed by:* J. A. Elvidge, P. W. G. Smith.

Coleman, Lester Earl, jun., B.S. (Akron), M.S. and Ph.D. (Illinois). American. 4217, Brenau Avenue, Apt. 3, Dayton 9, Ohio, U.S.A. Project Engineer and Research Chemist, U.S. Air Force. *Signed by:* H. Rosenberg, J. F. O'Brien.

Corran, John Anthony, B.Sc. (Liv.), A.R.I.C. British. 13, Boundary Drive, Hunts Cross, Woolton, Liverpool. Research Student at Liverpool University. *Signed by:* A. Mee, D. A. H. Taylor.

Crimmin, William Robert Charles, B.Sc. and Ph.D. (Wales), A.R.I.C. British. Lister Institute of Preventive Medicine, Chelsea Bridge Road, London, S.W.1. Research Assistant. *Signed by:* G. M. Gray, S. A. Warsi.

Culling, Gerald Charles. British. 24, Aintree Crescent, Barkingside, Ilford, Essex. Student. *Signed by:* J. P. Jones, T. J. Barnes.

Davies, David Rowland. British. 33, Brook Street, Luton, Beds. Student at Queen Mary College. *Signed by:* K. W. Sykes, T. R. Layzell.

Despic, Alexander, Ph.D. (Lond.), D.I.C. Yugoslav. Carla Caplina 38, Beograd, Yugoslavia. University Assistant. *Signed by:* G. J. Hills, J. A. Kitchener.

Dinwoodie, Andrew Harper, B.A. (Cantab.). British. 32, Swinburne Street, Derby. Research Student. *Signed by:* R. N. Haszeldine, D. W. A. Sharp.

Dunstan, Francis Elliott. British. The Union, Edgbaston Park Road, Birmingham, 15. Student at Birmingham University. *Signed by:* J. C. Tatlow, J. Sheridan.

Feltham, Robert Dean, B.S. (New Mexico). American. 926, Gill Court, Albany 6, California, U.S.A. Student at California University, *Signed by:* M. Calvin, M. Look.

Fischer, Albert Karl, M.A. (Harvard). American. Perkins Hall, Room 47, Harvard University, Cambridge 38, Massachusetts, U.S.A. Graduate Student. *Signed by:* H. D. Kaesz, F. G. A. Stone.

Gardner, Joan Dorothea. British. 55, Links Road, Tooting, London, S.W.17. Secretary and Research Assistant in Printing and Paper Technology. *Signed by:* L. G. Luker, D. M. Freeland.

Godin, Peter John, B.Sc. (Lond.), A.R.C.S. British. 53, Colbourne Way, Worcester Park, Surrey. Research Student at Imperial College. *Signed by:* L. Crombie, J. A. Elvidge.

Goodgame, David Martin Lawrence. British. Great Hill Plantation, Wigginton, Nr. Tring, Herts. Student. *Signed by:* R. E. Richards, D. E. Hayler.

Hamied, Yusuf K. Indian. Christ's College, Cambridge. Student. *Signed by:* R. N. Haszeldine, P. Maitland.

Hardegger, Emil. Swiss. Lufingen (ZH), Zwitzerland. Professor of Organic Chemistry. *Signed by:* B. G. Engel, L. Ruzicka.

Harris, Adelaide, M.Sc. (Liv.), A.R.I.C. British. 23, Archerfield Road, Liverpool, 18. Demonstrator at Liverpool University. *Signed by:* W. B. Whalley, A. McGookin.

Huitric, Alain C., Ph.D. (California). American. College of Pharmacy, University of Washington, Seattle 5, Washington, U.S.A. Assistant Professor. *Signed by:* H. J. Dauben, A. G. Anderson.

Kennedy, Thomas, B.Sc. (Glas.). British. 58, Dunchurch Road, Oldhall, Paisley, Renfrewshire. University Demonstrator. *Signed by:* D. S. Payne, J. Bell.

Kettle, Sidney Francis Alan, B.Sc. (Leeds). British. The University Chemical Laboratories, Lensfield Road, Cambridge. Research Student. *Signed by:* R. N. Haszeldine, J. D. Smith.

Lightman, Paul. British. 66, Finchley Court, Ballards Lane, Finchley, London, N.3. Student. *Signed by:* W. J. Hickinbottom, K. W. Sykes.

Lubienski, Andrzaj Maria, B.Sc. (Lond.). Polish. 10, Auriol Mansions, London, W.14. Research Student at Acton Technical College. *Signed by:* P. H. Gore, S. C. Bevan.

Massey, Alan Gibbs. British. 33, Ripon Road, Ansdell, Lytham-St. Annes, Lancs. Student at Liverpool University. *Signed by:* A. K. Holliday, A. Hickling.

Morison, Elizabeth Ann, B.A. (Oxon). British. 57, Evelyn Gardens, London, S.W.7. Chemist with J. Lyons & Co., Ltd. *Signed by:* H. W. Thompson, M. L. Tomlinson.

McCaffery, Edward Lawrence, B.S. (St. Johns Univ.), M.S. and Ph.D. (Maryland). American. 3500, Grays Ferry Avenue, Philadelphia, Pennsylvania, U.S.A. Research Chemist with E.I. du Pont Co. *Signed by:* J. R. Chalmers, J. Blake.

McCauley, Charles Edward, A.B. and M.S. (Georgetown), M.S. and Ph.D. (New York). American. Chemistry Department, St. Peter's College, 2641, Hudson Boulevard, Jersey City 6, N.J., U.S.A. Associate Professor. *Signed by:* A. P. Wolf, N. Sutin.

McIver, Edward James. British. Waverley, Cheviot View, Ponteland, Newcastle upon Tyne. Student at Durham University. *Signed by:* K. H. Jack, F. J. McQuillin.

Nixon, Joseph Robert, B.Pharm. (Lond.). British. 10, Narborough Street, London, S.W.6. Research Student at Chelsea Polytechnic. *Signed by:* B. A. Mulley, A. H. Beckett.

Osborne, Edgar Howard, B.Sc. (Liv.). British. 7, Kenwardly Road, Willerby, Hull. Research Student at Hull University. *Signed by:* K. Clarke, G. W. Gray.

Osborne, Graham Oliver, B.Sc. and Ph.D. (Wales), A.R.I.C. British. Department of Organic Chemistry, Kings College, Newcastle upon Tyne. Research Assistant. *Signed by:* J. Baddiley, J. G. Buchanan.

Pauling, Peter Jeffress, B.Sc. (C.I.T.). American. 21, Albemarle Street, London, W.1. Student. *Signed by:* J. D. Dunitz, R. S. Nyholm.

Phinister, George, B.Sc. (Aberd.). British. Colombo Commercial Co., Ltd., P.O. Box 33, Colombo, Ceylon. Analyst. *Signed by:* M. U. S. Sultanbawa, G. P. Wannigama.

Price, Diana Rosemary West, B.Sc. (St. Andrews). British. Rowsley, Ryhall, Stamford, Lincolnshire. Research Chemist with Albright & Wilson, Ltd., Birmingham. *Signed by:* D. P. Elias, D. E. C. Corbridge.

Reynolds, George Egerton, B.Sc. (Reading). British. 24, Erroll Road, Romford, Essex. *Signed by:* P. F. Holt, L. C. Cross.

Slade, Peter, M.Sc. (Lond.). British. 85, Craven Gardens, Barkingside, Ilford, Essex. Research Student. *Signed by:* D. H. Hey, H. B. Henbest, M. C. Dart.

Slinger, James Brian, B.Sc. (Sheffield). British. 76, Clarke Grove Road, Sheffield 10. Research Student. *Signed by:* K. Jewers, B. F. Hallam.

Smith, Brian Cyril. British. Needler Hall, Cottingham, East Yorkshire. Student at Hull University. *Signed by:* J. Shorter, G. W. Gray.

Street, Colin Arthur. British. 15, Glenhurst Road, Prittlewell, Essex. Student at University College, Leicester. *Signed by:* E. R. A. Peeling, S. H. Harvey.

Swinton, Herbert Donald. British. 27, Rufford Road, Edwinstown, Mansfield, Notts. Student at Hull University. *Signed by:* G. W. Gray, G. C. Bond.

Tolliday, Joan Margaret, M.A. (Cantab.). British. Birkbeck College Research Laboratories, 21, Torrington Square, London, W.C.1. Research Assistant. *Signed by:* P. G. Owston, J. Chatt.

Turner, James Bryan, B.Sc. (Lond.), A.R.I.C. British. 17, Worcester Place, Oxford. Research Student at Oxford University. *Signed by:* M. V. Kelemen, R. B. Clayton.

Walker, Graham Peter. British. 299, Bramhall Lane South, Bramhall, Cheshire. Student. *Signed by:* J. J. Kipling, G. W. Gray.

White, George Raymond. British. c/o 2A, Forthbridge Road, Clapham Common, S.W.11. Student at Imperial College. *Signed by:* J. A. Elvidge, G. Lowe.

Wright, Graham Allen, B.Sc. (New Zealand). British. Chemistry Department, University College, Auckland, New Zealand. Student. *Signed by:* A. L. Odell, T. A. Turney.

UNDER SPECIAL PROVISION APPERTAINING TO CANDIDATES RESIDENT ABROAD.

Durso, Donald F., Ph.D. (Purdue). American. 3281, Kimball Avenue, Memphis 11, Tennessee, U.S.A. Associate Director of Buckeye Cellulose Corp. *Signed by:* A. M. Dowell, jun.

Gritter, Roy John, A.B. (Calvin Coll.), Ph.D. (Chicago). American. Department of Chemistry, University of Connecticut, Storrs, Connecticut, U.S.A. Instructor in Chemistry. *Signed by:* J. T. Stock.

Mohamed, Khaja Wali. Pakistani. c/o United Trading Company, Distributors, Ciba Dyestuffs Chemicals & Auxiliaries, 223, Jubilee Road, Chittagong, East Pakistan. Dyes and Chemicals Distributor. *Signed by:* K. S. Mohamad.

Pradhan, Pratap Krishnarao. Indian. Avadhut Bhuvan, Sitabaldi, Nagpur, India. Chief Chemist of Irvo Laboratory. *Signed by:* M. K. Pradhan.

Satyanarayana, Mukkavilli, M. Pharm. (Andhra). Indian. Department of Pharmacy, Andhra University, Waltair, S. India. Research Scholar. *Signed by:* S. K. Pavanaram.

Thompson, William Alexander Brown, B.Sc. (St. Andrews). British. c/o Biochemistry Department, University of Wisconsin, Madison 6, Wisconsin, U.S.A. Research Assistant and Graduate Student at Wisconsin University. *Signed by:* W. S. Johnson.

Wylde, James Paxton d'Eglesfield, M.A. (Cantab.). British. Institut de Chimie, 8, Rue de L'Ecole Normale, Montpellier, Hérault, France. Research Student. *Signed by:* M. Mousseron.

Correction.

In the Proceedings for August, 1956, p. 92, Mr. Miller was incorrectly described as a Pharmacist.

PAPERS ACCEPTED

(List of Papers accepted between September 18th and October 18th, 1956, for publication in the *Journal.*)

"Fading and tendering activity in anthraquinonoid vat dyes. Part I. Electronic absorption spectra of dye solutions." By J. J. Moran and H. I. Stonehill.

"Ion-exchange studies of phosphates. Part II. Phosphoric acid as an eluant in the column separation of tervalent iron from bivalent copper and manganese." By J. A. R. Genge and J. E. Salmon.

"The structure of molecular compounds. Part XI. Crystal structure of the addition complex of quinol and methyl cyanide." By S. C. Wallwork and H. M. Powell.

"The structure and chemistry of geigerin." By G. W. Perold.

"The equilibrium in the system: Water–6-hexanolactam (ε-caprolactam)." By A. B. Meggy.

"Search for spectral evidence of expansion of the valency shell of sulphur in aromatic sulphides." By A. Mangini and R. Passerini.

"Adsorption spectra in the near-ultraviolet region of some thiolsulphonates." By G. Leandri, A. Mangini, and A. Tundo.

" Synthesis of cyclic hydrocarbons. Part I. *o*-Dialkylbenzenes." By B. B. ELSNER, H. E. STRAUSS, and E. J. FORBES.

" Synthesis of cyclic hydrocarbons. Part II. Dehydrogenation of 1 : 2-dialkyl*cyclo*hexanes to *o*-dialkylbenzenes." By B. B. ELSNER and H. E. STRAUSS.

" Synthesis of cyclic hydrocarbons. Part III. 1 : 2-Dialkyl*cyclo*hexanes." By B. B. ELSNER and H. E. STRAUSS.

" Synthesis of cyclic hydrocarbons. Part IV. Alkylindanes." By B. B. ELSNER and K. J. PARKER.

" Reactions of organic peroxides. Part VIII. 1 : 3 : 3-Trimethylindan-1-yl hydroperoxide and its conversion into 2 : 4 : 4-trimethylchroman derivatives." By W. WEBSTER and D. P. YOUNG.

" *d*-Orbital contraction in chemical bonding." By D. P. CRAIG and E. A. MAGNUSSON.

" Kinetics and mechanism of bromination of phenol with bromine and iodine bromide in glacial acetic acid and carbon tetrachloride." By LOURDU M. YEDDANAPALLI and N. S. GNANAPRAGASAM.

" Chemical action of ionising radiations. Part XVII. Degradation of deoxyribonucleic acid in aqueous solution by irradiation with *X*-rays (200 kv)." By M. DANIELS, G. SCHOLES, J. WEISS, and C. M. WHEELER.

" The structure of the dimer of thiocarbonyl chloride and its hydrolysis product. Infrared absorption data on some compounds containing the thiocarbonyl group." By J. IDRIS JONES, W. KYNASTON, and J. L. HALES.

" The infrared absorption spectra of some chloroformates and carbonates. The structure of di- and tri-phosgene." By J. L. HALES, J. IDRIS JONES, and W. KYNASTON.

" Electrophilic substitution. Part VII. Rates of chlorination of aromatic hydrocarbons." By M. J. S. DEWAR and T. MOLE.

" The action of Grignard reagents on dianthron-9-ylidene and dianthron-9-yl." By ABDEL FATTAH ALY ISMAIL and ZAKI MOHAMMED EL-SHAFEI.

" Electric dipole moment studies. Part II. The dielectric polarisation of cyclic ethers in the vapour phase." By W. L. G. GENT.

" The interaction of aldehydes with boron trichloride." By M. J. FRAZER, W. GERRARD, and M. F. LAPPERT.

" Chemical action of ionising radiations in solution. Part XVIII. Action of *X*-rays (200 kv) on α- and β-glycerophosphate in aqueous solution." By G. SCHOLES, W. TAYLOR, and J. WEISS.

" Solvent quenching of fluorescence." By E. J. BOWEN and D. M. STEBBENS.

" Promoters for the dropwise condensation of steam. Part I. Preparation of compounds containing monofunctional sulphur groups." By L. C. F. BLACKMAN and M. J. S. DEWAR.

" Promoters for the dropwise condensation of steam. Part II. Preparation of compounds containing polyfunctional sulphur groups." By L. C. F. BLACKMAN and M. J. S. DEWAR.

" Promoters for the dropwise condensation of steam. Part III. Preparation of silicon and phosphorus compounds." By L. C. F. BLACKMAN and M. J. S. DEWAR.

" Promoters for the dropwise condensation of steam. Part IV. Discussion of dropwise condensation and testing of compounds." By L. C. F. BLACKMAN, M. J. S. DEWAR, and H. HAMPSON.

" Complexes of a ditertiary arsine with univalent and tervalent gold." By C. M. HARRIS and R. S. NYHOLM.

" Researches on acetylenic compounds. Part LIII. The relative strengths of some unsaturated carboxylic acids." By G. H. MANSFIELD and M. C. WHITING.

" The structure and reactivity of 2-aminopyridine 1-oxide." By A. R. KATRITZKY.

" The *cis*- and *trans*-αβ-dicyanostilbenes. Part I. The geometrical configuration and cyclisation of the *trans*-isomer, the previously alleged diphenylmaleidinitrile." By D. G. COE, M. M. GALE, R. P. LINSTEAD, and C. J. TIMMONS.

" Oxidations with phenyl iodosoacetate. Part VI. The oxidation of some phenols containing electron-attracting substituents." By A. R. FOX and K. H. PAUSACKER.

" Perfluoroalkyl derivatives of nitrogen. Part V. The mechanism of the Hofmann reaction with amides containing electronegative groups." By D. A. BARR and R. N. HASZELDINE.

" Interaction of boron trichloride with alkyl chloro-alkyl ethers." By J. D. EDWARDS, W. GERRARD, and M. F. LAPPERT.

" Surface force and stability of lecithin sols." By P. H. ELWORTHY and L. SAUNDERS.

" The decarboxylative acylation of succinic acid derivatives. Part II. *o*-Hydroxyphenylsuccinic, tricarballylic, and thiobenzamidosuccinic acids." By ALEXANDER LAWSON.

" The condensation of azomethines with hydrogen sulphide and aldehydes." By D. COLLINS and J. GRAYMORE.

" Red-seaweed polysaccharides. Part I. *Gracilaria confervoides*." By A. L. CLINGMAN, J. R. NUNN, and A. M. STEPHEN.

" Coenzyme A. Part X. Model experiments on the synthesis of pyrophosphates of *N*-pantoylamines. New methods for the debenzylation of esters of pyrophosphoric acid." By J. ARRIS, J. BADDILEY, J. G. BUCHANAN, and E. M. THAIN.

" Sesquiterpenoids. Part VIII. The constitution of pyrethrosin." By D. H. R. BARTON and P. DE MAYO.

" Chemical action of ionising radiations in solution. Part XIX. Some aspects of the reduction of methylene-blue by *X*-rays in aqueous systems." By E. HAYON, G. SCHOLES, and J. WEISS.

" 3-Hydroxythiophen." By M. C. FORD and DONALD MACKAY.

" Exchange of chlorine-36 between chloride ion and phosphorous oxychloride, arsenic trichloride, or selenium oxychloride." By J. LEWIS and D. B. SOWERBY.

" The action of lime water on 3-*O*-methyl-D-xylose." By W. M. CORBETT, G. N. RICHARDS, and ROY L. WHISTLER.

" Studies on biological methylation. Part XVI. Natural sulphonium compounds. The alkyl methyl sulphides evolved from the urine of dogs by boiling alkali." By DEREK LEAVER and FREDERICK CHALLENGER.

" The interaction of alkylbenzenes with excess of Friedel–Crafts acetylating agent." By G. BADDELEY and E. WRENCH.

" Oxygen heterocycles. Part VII. Spasmolytic ketones in the benzofuran series and related compounds." By NG. PH. BUU-HOÏ, E. BISAGNI, R. ROYER, and C. ROUTIER.

" The fission of alkyl allyl ethers by boron trichloride." By W. GERRARD, M. F. LAPPERT, and H. B. SILVER.

" Diaryl-2 : 2'-disulphonic acids and related compounds. Part III. Optical activity and optical stability in the 1 : 1'-dinaphthyl series." By W. L. F. ARMAREGO and E. E. TURNER.

" A molecular rearrangement during the reduction of thionaphthenopyrazole dioxides." By W. J. BARRY, I. L. FINAR, and ALMA B. SIMMONDS.

" The activation of carbon–carbon double bonds by cationic catalysts. Part III. The coloured species formed by the interaction of 1 : 1-di-*p*-methoxyphenylethylene with trichloroacetic acid in benzene." By ALWYN G. EVANS, PETER M. S. JONES, and J. H. THOMAS.

" Synthetic plant hormones. Part IV. Aryloxymethane phosphonous acids." By (MISS) M. H. MAGUIRE and G. SHAW.

" Reversible and irreversible adsorption of vapours by solid oxides and hydrated oxides." By J. J. KIPLING and D. B. PEAKALL.

" The kinetics and mechanisms of aromatic halogen substitution. Part III. Partial rate factors for the acid-catalysed bromination of *tert.*-butylbenzene by hypobromous acid." By P. B. D. DE LA MARE and J. T. HARVEY.

" Complex fluorides. Part VIII. The preparation and properties of salts of the triphenylmethyl cation : The infrared spectrum and configuration of the ion." By D. W. A. SHARP and N. SHEPPARD.

" Structure and reactivity of the oxyanions of transition metals. Part III. The hypochromate ion." By N. BAILEY and M. C. R. SYMONS.

" Amino-sugars and related compounds. Part II. Observations on the acidic hydrolysis of derivatives of 2-amino-2-deoxy-D-glucose (D-glucosamine)." By A. B. FOSTER, D. HORTON, and M. STACEY.

" The action of light on normal and *iso*-diazoates." By R. J. W. LE FÈVRE and J. B. SOUSA.

" Molecular polarisability. The molar Kerr constants, apparent dipole moments, and dielectric absorptions of certain substances showing unusual atomic polarisations." By R. S. ARMSTRONG, (MRS.) C. G. LE FÈVRE, and R. J. W. LE FÈVRE.

" Nucleotides. Part XL. O^2 : 5'-*cyclo*Uridine and a synthesis of *iso*cytidine." By D. M. BROWN, SIR ALEXANDER TODD, and S. VARADARAJAN.

" The preparation and properties of certain alkoxychloroboron chlorides and tri(chloroalkyl) borates." By E. W. ABEL, J. D. EDWARDS, W. GERRARD, and M. F. LAPPERT.

" Purine studies. Part III. The structure of the monohydroxy- and monomercaptopurines : Some thiazolo(5 : 4-*d*)pyrimidines." By D. J. BROWN and S. F. MASON.

" Studies of a cross-linked poly(ethyleneimine) ion-exchange resin." By E. J. SHEPHERD and J. A. KITCHENER.

" The preparation of esters of diphenylboronous acid." By E. W. ABEL, W. GERRARD, and M. F. LAPPERT.

" Dipole moments and molecular structure. Part II. Pentaerythritol tetranitrate." By C. T. MORTIMER, H. SPEDDING, and H. D. SPRINGALL.

" Organic nitrates. Part I. Diphenylmethyl nitrate." By G. W. H. CHEESEMAN.

" Chemical constitution and the dissociation constants of monocarboxylic acids. Part XVI. Some acylbenzoic acids." By L. G. BRAY, J. F. J. DIPPY, and S. R. C. HUGHES.

" The reactivity of the *O*-acylglycosyl halides. Part V. The catalysed and uncatalysed solvolysis of 1 : 2-*trans*-*O*-acetylglycosyl halides." By G. L. MATTOK and G. O. PHILLIPS.

" The formation of iodine cations. Part I. Magnetic evidence." By M. C. R. SYMONS.

" Electron-donor and -acceptor complexes with aromatic systems. Part III. Absorption spectra of some benzoquinolines and of their complexes with bromine in solution." By W. SLOUGH and A. R. UBBELOHDE.

" Fading and tendering activity in anthraquinonoid vat dyes. Part II. Fluorescence, absorption spectra, and stability to light of dyed films." By J. J. MORAN and H. I. STONEHILL.

" Fading and tendering activity in anthraquinonoid vat dyes. Part III. Free-radical production and probable reaction mechanisms." By J. J. MORAN and H. I. STONEHILL.

" Synthesis of new sugar derivatives of potential antitumour activity. Part I. Ethyleneimino- and 2-chloroethylamino-derivatives." By L. VARGHA, L. TOLDY, O. FEHER, and S. LENDVAI.

" Synthesis of new sugar derivatives of potential antitumour activity. Part II. *N*-Di-(2-chloroethyl)-D-glucosamine hydrochloride." By L. VARGHA, O. FEHER, and S. LENDVAI.

" Synthesis of *meso*tetramethylchlorin." By ULLI EISNER.

" Organosilicon compounds. Part XVIII. The interaction of (aryldimethylsilyl)-methyl chlorides and sodium ethoxide in ethanol." By C. EABORN and J. C. JEFFREY.

" Dynamic contact angles. Part I. Changes in air–solution–solid contact angles with time." By T. A. ELLIOTT and L. LEESE.

" The synthesis of methyl- and dimethyl-dibenzofurans." By S. TRIPPETT.

" The formation of carbonium ions by the action of metal salts. Part III. The reaction of mercuric chloride with triarylmethyl chlorides in nitromethane, chlorobenzene, and benzene." By J. W. BAYLES, ALWYN G. EVANS, and J. R. JONES.

" Electron-donor and -acceptor complexes with aromatic systems. Part IV. An improved method of preparing metal addition complexes with aromatic systems." By W. SLOUGH and A. R. UBBELOHDE.

" Chemistry of micrococcin P. Part I." By P. BROOKES, A. T. FULLER, and JAMES WALKER.

" Mesomorphism and chemical constitution. Part VIII. The effect of 3'-substituents on the mesomorphism of the 4'-*n*-alkoxydiphenyl-4-carboxylic acids and their alkyl esters." By G. W. GRAY, BRYNMOR JONES, and F. MARSON.

" The parallelism of the acidity functions H_0 and H_-." By T. G. BONNER and J. C. LOCKHART.

" Steric effects in the oxidation of hexitols with periodate." By J. C. P. SCHWARZ.

" The constituents of high-boiling petroleum distillates. Part IV. Some polycyclic aromatic hydrocarbons in a Kuwait oil." By W. CARRUTHERS and A. G. DOUGLAS.

" An antibiotic similar to xanthomycin A." By D. K. DOUGALL.

" The degradation of xylobiose and xylotriose by alkali." By G. O. ASPINALL, (MISS) MARY E. CARTER, and (in part) M. LOS.

" Conjugated macrocycles. Part XXVIII. Adducts from di-imino*iso*indoline and arylene-*m*-diamines, and a new type of cross-conjugated macrocycle with three-quarters of the chromophore of phthalocyanine." By J. A. ELVIDGE and J. H. GOLDEN.

" Heterocyclic imines and amines. Part VIII. Identification of " *o*-cyanothiobenzamide " as 1-imino-3-thio*iso*indoline, and its conversion with amines into macrocycles and intermediates." By M. E. BAGULEY and J. A. ELVIDGE.

" Structural aspects of the hydrolysis of titanium alkoxides." By D. C. BRADLEY, R. GAZE, and W. WARDLAW.

" Studies of trifluoroacetic acid. Part XIII. Cryoscopic measurements on trifluoroacetic anhydride–acetic acid systems." By E. J. BOURNE, J. C. TATLOW, and R. WORRALL.

" The chemistry of the ' insoluble red ' woods. Part VII. The synthesis of coumarino(3' : 4'-3 : 2)coumarones." By W. J. BOWYER, ALEXANDER ROBERTSON, and W. B. WHALLEY.

" Lipids. Part IV. Synthesis of branched-chain fatty acids." By L. CROMBIE, M. MANZOOR-I-KHUDA, and R. J. D. SMITH.

" Lipids. Part V. Total synthesis of ximenynic acid, homoricinstearolic acid, and two fatty hydroxy-acids with allenic side-branches." By L. CROMBIE and A. G. JACKLIN.

" Lipids. Part VI. Total synthesis of α- and β-elæostearic and punicic (trichosanic) acid." By L. CROMBIE and A. G. JACKLIN.

" The Ehrlich–Sachs reaction." By F. BELL.

" Germanium esters. Part I. Parachors and molecular structure." By D. C. BRADLEY, L. J. KAY, and W. WARDLAW.

" The synthesis of indenoquinolines." By NEIL CAMPBELL and ARTHUR F. TEMPLE.

" Kinetics of the reaction between ethyl iodomalonate and iodide ions." By R. P. BELL and P. ENGEL.

" Derivatives of 2 : 4-dioxo-3-phenylacetamidobutanoic acid." By J. W. CORNFORTH and (MRS.) R. H. CORNFORTH.

" Thermodynamics of ion association. Part III. Some thallous-ion pairs with univalent anions." By V. S. K. NAIR and G. H. NANCOLLAS.

" The reactions of acridine and 5-phenylacridine with benzyl radicals." By W. A. WATERS and D. H. WATSON.

" Quinoxaline derivatives. Part III. Cyclisation of 3 : 4-dihydro-3-oxoquinoxaline-2-carboxyureides to 1 : 2 : 3 : 4-tetrahydro-3-oxoquinoxaline-2-*spiro*-5'-hydantoins." By J. W. CLARK-LEWIS.

" Quinoxaline derivatives. Part IV. Dihydro-oxo-1 : 4 : 5-triazanaphthalenecarboxyureides and related spirohydantoins." By J. W. CLARK-LEWIS and M. J. THOMPSON.

" Quinoxaline derivatives. Part V. Decomposition of 3 : 4-dihydro-4-methyl-3-oxoquinoxaline-2-carboxymethylanilide 1-oxide with sulphuric acid." By J. W. CLARK-LEWIS.

" Methylation of 3-aminopyridines and preparation of 2-amino-3-methylaminopyridine and 2 : 3-diaminopyridine." By J. W. CLARK-LEWIS and M. J. THOMPSON.

" Carcinogenic nitrogen compounds. Part XXI. New alkyl homologues of phenanthridine, benzacridines, and related nuclei." By NG. PH. BUU-HOÏ, P. JACQUIGNON, and C. T. LONG.

" Conductimetric studies in ketonic solvents." By S. R. C. HUGHES.

" The basis of the selectivity of dimethylglyoxime as a reagent in gravimetric analysis." By A. G. SHARPE and D. B. WAKEFIELD.

" The action of hydrogen chloride on the nickel and palladium derivatives of dimethylglyoxime." By A. G. SHARPE and D. B. WAKEFIELD.

" Reactions in boron trichloride–cyclic ether systems." By J. D. EDWARDS, W. GERRARD, and M. F. LAPPERT.

" Researches on polyenes. Part V. The synthesis of cortisalin." By D. MARSHALL and M. C. WHITING.

" New synthesis of 2 : 3-dihydro-1-oxopentindole." By K. F. JENNINGS.

" Organosilicon compounds. Part XX. Trimethyl-*p*-nitrophenylsilane." By F. B. DEANS and C. EABORN.

" The bromination of 8-methoxyquinaldine." By H. IRVING and A. R. PINNINGTON.

" Some bromine-substituted derivatives of 8-hydroxyquinoline." By H. IRVING and A. R. PINNINGTON.

" The organic chemistry of phosphorus. Part IV. The thermal decomposition of tetra-aryloxyphosphorus monohalides : a new method for the preparation of aryl halides." By D. G. COE, H. N. RYDON, and B. L. TONGE.

" Carbohydrates of the seeds of the rubber tree, *Hevea brasiliensis*." By D. M. W. ANDERSON, C. T. GREENWOOD, and J. S. M. ROBERTSON.

" Studies of the coal-tar bases. Part VI. A new synthesis of 3 : 5-lutidine." By E. A. COULSON and J. B. DITCHAM.

" 3-Hydroxyphenylpyruvic acid." By R. M. ACHESON.

" Alkyl bisdialkylaminoboronites and related compounds." By W. GERRARD, M. F. LAPPERT, and C. A. PEARCE.

" Solvent extraction studies with polonium." By K. W. BAGNALL and D. S. ROBERTSON.

" The cyclisation of 1 : 8-di- and 1 : 4 : 5 : 8-tetra-(α-anthraquinonylamino)anthraquinone to derivatives of carbazole." By WILLIAM BRADLEY and P. N. PANDIT.

" Equivalence changes in oxidation-reduction reactions in solution; some aspects of the oxidation of sulphurous acid." By W. C. E. HIGGINSON and J. W. MARSHALL.

" Thionaphthen 1 : 1-dioxide as a dienophil." By W. DAVIES and Q. N. PORTER.

" Autoxidation of polyphenols. Part I. Autoxidation of methyl gallate and its *O*-methyl ethers in aqueous ammonia." By D. E. HATHWAY.

" The constitution of *apo*galanthamine." By SHIGERU KOBAYASHI and SHOJIRO UYEO.

" Tritium-labelled 2-methyl-1 : 4-naphthaquinone and confirmation of the structure of its adduct with sodium hydrogen sulphite." By D. H. MARRIAN.

" The action of nitrosyl chloride on certain silicates." By I. R. BEATTIE.

" The degradation of carbohydrates by alkali. Part XIV. 3 : 6-Anhydro-D-glucose." By W. M. CORBETT and J. KENNER.

" The effect of solvent on a simple ion–dipole reaction. Part 2. The rate of the methyl iodide–iodide ion exchange in five different solvents." By E. R. SWART and L. J. LE ROUX.

" Extension of the Diels–Alder reaction to monocyclic benzenes : Addition of maleic anhydride to quinol." By R. C. COOKSON and N. S. WARIYAR.

" Studies in relation to biosynthesis. Part IX. The structure of spherophysine." By A. J. BIRCH, D. G. PETTIT, and R. SCHOFIELD.

" Studies in relation to biosynthesis. Part X. A synthesis of lumichrome from non-benzenoid precursors." By A. J. BIRCH and C. J. MOYE.

" Addition compounds of gallium trichloride. Part II. Gallium trichloride–phosphorus oxychloride." By N. N. GREENWOOD and K. WADE.

" An investigation of the Gibbs reaction and its bearing on the constitution of jacareubin." By F. E. KING, T. J. KING, and L. C. MANNING.

" Synthesis of (±)-ophiocarpine." By T. R. GOVINDACHARI and S. RAJADURAI.

" Chemical investigation of *Wedelia calendulacea*. Part II. The position of the methoxyl group in wedelolactone." By T. R. GOVINDACHARI, K. NAGARAJAN, B. R. PAI, and P. C. PARTHASARATHY.

" Adsorption from binary liquid mixtures on silicic acid gel. Part I." By D. C. JONES and G. S. MILL.

" Hydrolysis of amides and related compounds. Part II. Acetylglycine, piperazine-2 : 5-dione, and gelatin in concentrated hydrochloric acid." By J. T. EDWARD and S. C. R. MEACOCK.

" The rearrangement of furfuryl alcohol to methyl lævulate." By K. G. LEWIS.

" The addition of ethyl diazoacetate to sorbic esters : a correction." By MARTIN G. ETTLINGER, S. H. HARPER, and FLYNT KENNEDY.

" The preparation of 9 : 10-di-(4-carboxybutyl)anthracene and related reactions." By K. JASPER CLARK.

" Chemical examination of *Wedelia calendulacea*. Part III. Synthesis of tri-*O*-methylwedelolactone." By T. R. GOVINDACHARI, K. NAGARAJAN, and P. C. PARTHASARATHY.

" Some degradation studies of carpaine." By T. R. GOVINDACHARI, N. S. NARASIMHAN, and S. RAJADURAI.

" Synthesis of ethyl carpyrinate." By T. R. GOVINDACHARI, N. S. NARASIMHAN, and S. RAJADURAI.

" Structure and reactivity of the oxyanions of transition metals. Part IV. Some relations between electronic spectra and structure." By A. CARRINGTON, D. SCHONLAND, and M. C. R. SYMONS.

" The quinquevalent fluororhenates." By R. D. PEACOCK.

ADDITIONS TO THE LIBRARY

Training of literature chemists : papers presented before the Division of Chemical Education and the Division of Chemical Literature at the 127th national meeting of the American Chemical Society, Cincinnati, 1955. (Advances in Chemistry Series, No. 17.) American Chemical Society. 1956.

A key to pharmaceutical and medicinal chemistry literature : papers presented before the Divisions of Chemical Literature and Medicinal Chemistry at the 124th and 126th national meetings of the American Chemical Society, 1953 and 1954. (Advances in Chemistry Series, No. 16.) American Chemical Society. 1956.

Medicinal chemistry, edited by F. F. Blicke and C. M. Suter. Vol. II. A series of reviews prepared under the auspices of the Division of Medicinal Chemistry of the American Chemical Society. John Wiley & Sons, Inc. 1956.

1955 Book of ASTM standards including tentatives. 7 Parts and index. American Society for Testing Materials. 1955—56.

Polyesters and their applications, by Bjorksten Research Laboratories, Inc., J. Bjorksten, H. Tovey, B. Harker, and J. Henning. Reinhold Publ. Corp. 1956.

Transport processes in applied chemistry : the flow of physical properties in chemical reactors, by R. C. L. Bosworth. Sir Isaac Pitman and Sons, Ltd. 1956. (Presented by the Publishers.)

Flow of gases through porous media, by P. C. Carman. Butterworths Scientific Publications. 1956.

Valency and molecular structure, by E. Cartmell and G. W. A. Fowles. Butterworth Scientific Publications. 1956.

The chemistry and mode of action of plant growth substances; proceedings of a symposium held at Wye College, 1955; edited by R. L. Wain and F. Wightman. Butterworths Scientific Publications. 1956.

Cumming and Kay, quantitative chemical analysis, edited by R. A. Chalmers. 11th edn. Oliver and Boyd. 1956. (Presented by the Publishers.)

Androgens; biochemistry, physiology, and clinical significance, by R. I. Dorfman and R. A. Shipley. John Wiley & Sons, Ltd. 1956.

Catalysis. Vol. IV. Hydrocarbon synthesis, hydrogenation and cyclization, edited by P. H. Emmett. Reinhold Publ. Corp. 1956.

Annual review of physical chemistry, edited by H. Eyring, C. J. Christensen, and H. S. Johnston. Vol. 7. Annual Reviews, Inc. 1956. (Presented by the Publishers.)

Currents in biochemical research, 1956, edited by D. E. Green. Interscience Publishers, Inc. 1956.

Essays in biochemistry written in honor of Hans Thacher Clarke, edited by S. Graff. John Wiley & Sons, Inc. 1956.

Chemical safety supervision, by J. Guelich. Reinhold Publ. Corp. 1956.

Principles of fungicidal action, by J. G. Horsfall. Chronica Botanica Co. 1956.

Hutchison's food and the principles of dietetics; revised by V. H. Mottram and G. Graham. 11th edn. Edward Arnold Ltd. 1956.

The determination of toxic substances in air; a manual of I.C.I. practice, edited by N. Strafford, C. R. N. Strouts, and W. V. Stubbings, and produced by the Analytical Chemists' Committee of Imperial Chemical Industries Limited. Heffer. 1956.

Experimental thermochemistry; measurement of heats of reaction, edited by F. D. Rossini and prepared under the auspices of the International Union of Pure and Applied Chemistry by the Subcommission on Experimental Thermochemistry. Interscience Publishers, Inc. 1956.

Petroleum refining with chemicals, by V. A. Kalichevsky and K. A. Kobe. Elsevier. 1956.

Feinstruktur-untersuchungen an künstlichen Zellulosefasern verschiedener herstellungsverfahren. Teil 2. Der Kristallisationszustand. (Forschungsberichte des Wirtschafts- und Verkehrsministeriums Nordrhein-Westfalen. No. 261.) Westdeutscher Verlag. 1956. (Presented by the Publishers.)

Tables of physical and chemical constants and some mathematical functions, originally compiled by G. W. C. Kaye and T. H. Laby. Now prepared under the direction of an editorial committee, with Professor N. Feather as chairman. 11th edn. Longmans, Green and Co. 1956.

Thermochemical data of alloys, by O. Kubaschewski and J. A. Catterall. Pergamon Press. 1956.

The chemistry of cement and concrete, by F. M. Lea. 2nd edition of Lea and Desch. Edward Arnold Ltd. 1956.

Combustion processes, edited by B. Lewis, R. N. Pease, and H. S. Taylor. (High Speed Aerodynamics and Jet Propulsion. Volume II.) Oxford Univ. Press. 1956.

The chemistry of phenolic resins; the formation, structure, and reactions of phenolic resins and related products, by R. W. Martin. John Wiley & Sons, Inc. 1956.

Ion exchange technology, edited by F. C. Nachod and J. Schubert. Academic Press Inc. 1956.

The agricultural value of phosphate fertilisers which economise in the use of sulphuric acid; report on a study, by Dr. G. W. Cooke. Project No. 162. Organisation for European Economic Co-operation. European Productivity Agency. 1956. (Presented by the Publishers.)

Nouveau traité de chimie minérale; edited by Paul Pascal. Vol. X. Azote-Phosphore, by R. Dubrisay and P. Pascal. Masson et Cie. 1956. (Presented by the Publishers.)

Polyethylene, by R. A. V. Raff and J. B. Allinson. (High Polymers. Vol. XI.) Interscience Publishers, Inc. 1956.

Treatise on inorganic chemistry, by H. Remy. Translated by J. S. Anderson and edited by J. Kleinberg. Volume II. Subgroups of the periodic table and general topics. Elsevier. 1956.

Sodium: its manufacture, properties, and uses, by M. Sittig. (American Chemical Society Monograph Series, No. 133.) Reinhold Publ. Corp. 1956.

A life of Sir William Ramsay, by M. W. Travers. Edward Arnold Ltd. 1956.

Mass-transfer operations, by R. E. Treybal. McGraw-Hill. 1955.

Chromium. Vol. 1. Chemistry of chromium and its compounds, by M. J. Udy. (American Chemical Society Monograph Series No. 132.) Reinhold Publ. Corp. 1956.

Handbook of toxicology. Vol. I. Acute toxicities of solids, liquids and gases to laboratory animals, edited by W. S. Spector. Prepared under the direction of the Committee on the Handbook of Biological Data, Division of Biology and Agriculture, The National Academy of Sciences, The National Research Council. W. B. Saunders. 1956.

Technique of organic chemistry, edited by Arnold Weissberger. Vol. II. Catalytic reactions, photochemical reactions, and electrolytic reactions, by V. I. Komarewsky *et al.* 2nd edn. Interscience Publishers, Inc. 1956.

Proceedings of the Academy of Sciences of the U.S.S.R. Section: Chemical Technology. (Translation of section of *Doklady.*) 1956, Vol. 106, No. 1. (New periodical.) Consultants Bureau, Inc.

Proceedings of the Academy of Sciences of the U.S.S.R. Section: Chemistry. (Translation of section of *Doklady.*) 1956, Vol. 106, No. 1. (New periodical.) Consultants Bureau, Inc.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W. University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, M.A., D.Sc., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Ceylon.	M. U. S. Sultanbawa, B.Sc., Ph.D., A.R.I.C., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
,,	G. D. Meakins, M.A., D.Phil., Chemistry Department, The University, Manchester, 13.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham and Leicester	T. J. King, B.Sc., M.A., D.Phil., Chemistry Department, The University, University Park, Nottingham.
,,	E. R. A. Peeling, B.Sc., Ph.D., University College, Leicester.
Oxford.	R. E. Richards, M.A., D.Phil., Lincoln College, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	Miss Ishbel G. M. Campbell, B.Sc., Ph.D., Department of Chemistry, The University, Southampton.
South Wales.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.
,,	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY

SCIENTIFIC MEETINGS DURING FEBRUARY, 1957

LONDON.

Thursday, February 14th, 1957, at 7.30 p.m.

Pedler Lecture, **The Course of Polar Reactions in Non-polar Conditions,** by Professor C. K. Ingold, D.Sc., F.R.I.C., F.R.S. To be given in the Lecture Theatre, The Royal Institution, Albemarle Street, W.1.

Thursday, February 28th, at 7.30 p.m.

Lecture, **Application of Acidity Functions to the Mechanism of Acid Catalyzed Reactions,** by Professor F. A. Long. To be given in the Rooms of the Society, Burlington House, W.1.

ABERDEEN.

Thursday, February 21st, 1957, at 7.30 p.m.

Lecture, **The Use of Photography in Scientific Investigations,** by Dr. J. F. Padday, B.Sc., D.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at Marischal College.

BIRMINGHAM.

Friday, February 8th, 1957, at 4.30 p.m.

Lecture, **Some Current Problems in Phase Transitions,** by Professor A. R. Ubbelohde, M.A., D.Sc., F.R.S. Joint Meeting with Birmingham University Chemical Society to be held in the Chemistry Department, The University.

BRISTOL.

Thursday, February 7th, 1957, at 5.15 p.m.

Lecture, **From Wallpaper to Crystals,** by Mr. F. Coles Phillips, M.A. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday, February 14th, at 7 p.m.

Lecture, **Free-radical Chemistry—A Survey,** by Professor D. H. Hey, D.Sc., Ph.D., F.R.I.C., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Department, The University.

Thursday, February 21st, at 5.15 p.m.

Lecture, **The Chemistry of Actinomycin**, by Professor A. W. Johnson, Ph.D., A.R.C.S. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

Thursday, February 28th, at 5.15 p.m.

Lecture, **Living Molecules**, by Professor J. D. Bernal, M.A., F.R.S. Joint Meeting with the Student Chemical Society to be held in the Chemistry Department, The University.

CAMBRIDGE.

Friday, February 1st, 1957, at 8.30 p.m.

Lecture, **The Control of Chemical Reactions in Living Cells**, by Professor H. A. Krebs, M.A., M.D., F.R.S. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Pembroke Street.

Monday, February 11th, at 8.30 p.m.

Lecture, **Reactions Kinetics in Acidic Media**, by Dr. V. Gold, B.Sc. To be given in the University Chemical Laboratory, Lensfield Road.

Friday, February 15th, at 8.30 p.m.

Lecture, **Some Recent Developments in the Chemistry of Metallic Surfaces**, by Professor K. W. Sykes, B.Sc., M.A., D.Phil. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Pembroke Street.

Friday, February 22nd, at 8.30 p.m.

Lecture, **Some Recent Studies in Relation to Biosynthesis**, by Professor A. J. Birch, D.Sc., D.Phil. Joint Meeting with the University Chemical Society to be held in the University Chemical Laboratory, Pembroke Street.

EDINBURGH.

Tuesday, February 5th, 1957, at 7.30 p.m.

Lecture, **Nucleotide Structure and Function,** by Professor J. Baddiley, D.Sc., Ph.D. Joint Meeting with the Royal Institute of Chemistry, Society of Chemical Industry, and Edinburgh University Chemical Society, to be held in the Biochemistry Lecture Theatre, Teviot Place.

Thursday, February 14th, at 7.30 p.m.

Lecture, **Lead Tetraethyl as an Engine Anti-knock,** by Professor A. D. Walsh, M.A., Ph.D. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Pharmaceutical Society Rooms, York Place.

EXETER.

Friday, February 8th, 1957, at 5 p.m.

Lecture, **Some Developments in Inorganic Stereochemistry,** by Professor R. S. Nyholm, D.Sc., Ph.D., F.R.I.C. To be given at the Washington Singer Laboratories, Prince of Wales Road.

GLASGOW.

Friday, February 15th, 1957, at 7 p.m.

Annual General Meeting of Local Fellows followed at 7.15 p.m. by a Meeting for the Reading of Original Papers. To be held in Room 24, Royal College of Science and Technology.

HULL.

Thursday, February 21st, 1957, at 6 p.m.

Lecture, **Polyesters and their Uses,** by Dr. H. Gudgeon, B.Sc., A.R.I.C. To be given in the Organic Lecture Theatre, The University.

IRISH REPUBLIC.

Wednesday, February 6th, 1957, at 7.45 p.m.

Lecture, **Co-catalysis in Friedel–Crafts Reactions,** by Dr. D. C. Pepper, M.A., F.I.C.I., M.R.I.A. To be given in the Chemistry Department, University College, Dublin.

LEEDS.

Thursday, February 7th, 1957, at 7 p.m.

Lecture, **Chocolates and Confectionery,** by Dr. F. H. Banfield, M.Sc., F.R.I.C. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held in the Chemistry Lecture Theatre, The University.

Monday, February 11th, at 7 p.m.

Society of Chemical Industry Lecture, **Organophosphorus Insecticides,** by Dr. B. A. Kilby, M.A., Ph.D., F.R.I.C. To be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

Monday, February 18th, at 6.30 p.m.

Royal Institute of Chemistry Lecture, **Silicones and their Industrial Applications,** by Mr. R. Nattrass, B.Sc. To be given in the Chemistry Lecture Theatre, The University. (All Fellows are invited.)

Monday, February 25th, at 6.30 p.m.

Lecture, **Steric Hindrance and Analytical Chemistry,** by Dr. H. M. N. H. Irving, M.A., F.R.I.C. Joint Meeting with Leeds University Union Chemical Society to be held in the Chemistry Lecture Theatre, The University.

LIVERPOOL.

Thursday, February 14th, 1957, at 5 p.m.

Lecture, **Metal Derivatives of *cyclo*Pentadiene,** by Professor G. Wilkinson, Ph.D., A.R.C.S. Joint Meeting with the University Chemical Society to be held in the Chemistry Lecture Theatre, The University.

Wednesday, February 27th, at 5 p.m.

Official Meeting and Pedler Lecture, **The Course of Polar Reactions in Non-polar Conditions,** by Professor C. K. Ingold, D.Sc., F.R.I.C., F.R.S. To be held in the Chemistry Lecture Theatre, The University.

MANCHESTER.

Friday, February 15th, 1957, at 6.30 p.m.

Lecture, **The Biosynthesis of Cholesterol,** by Dr. J. W. Cornforth, M.Sc., F.R.S. To be given in the Chemistry Lecture Theatre, The University.

NEWCASTLE AND DURHAM.

Monday, February 4th, 1957, at 5.15 p.m.

Lecture, **Electron Diffraction by Gases and its Chemical Application,** by Dr. L. E. Sutton, F.R.S. Joint Meeting with the Durham Colleges Chemical Society to be held in Lecture Room 239, University Science Laboratories, South Road, Durham.

Monday, February 18th, at 5.15 p.m.

Lecture, **The Study of Fast Reactions,** by Mr. R. P. Bell, F.R.S. Joint Meeting with the Durham Colleges Chemical Society to be held in Lecture Room 239, University Science Laboratories, South Road, Durham.

Friday, February 22nd, at 5.30 p.m.

Official Meeting and Lecture, **The Biological Synthesis of Oligosaccharides,** by Professor M. Stacey, Ph.D., F.R.I.C., F.R.S. To be held in the Chemistry Building, King's College, Newcastle upon Tyne.

NORTHERN IRELAND.

Thursday, February 21st, 1957, at 7.15 p.m.

Lecture, **The Study of very Rapid Reactions by the Methods of Flash Photolysis,** by Professor R. G. W. Norrish, Sc.D., F.R.I.C., F.R.S. Joint Meeting with the Royal Institute of Chemistry and the Society of Chemical Industry, to be held at the Queen's University, Belfast.

NORTH WALES.

Thursday, February 21st, 1957, at 5.45 p.m.

Lecture, **Some Aspects of the Structural Chemistry of Proteins and Nucleic Acids,** by Professor H. D. Springall, M.A., D.Phil., F.R.I.C. Joint Meeting with the University College of North Wales Chemical Society to be held in the Department of Chemistry, University College of North Wales, Bangor.

NOTTINGHAM AND LEICESTER.

Monday, February 18th, 1957, at 4.30 p.m.

Lecture, **Metal Atoms as Aromatic Systems,** by Dr. J. Chatt, M.A., F.R.I.C. Joint Meeting with the Chemical Society of the University College of Leicester to be held at University College, Leicester.

Tuesday, February 19th, at 4.45 p.m.

Lecture, **Organometallic Co-ordination Compounds,** by Professor G. E. Coates, D.Sc. Joint Meeting with Nottingham University Chemical Society to be held in the Chemistry Department, The University, Nottingham.

OXFORD.

Monday, February 4th, 1957, at 8.15 p.m.

Lecture, **Chemical and Physical Properties of Metal–Ammonia Solutions,** by Professor A. J. Birch, D.Sc., D.Phil. Joint Meeting with Oxford University Alembic Club to be held in the Physical Chemistry Laboratory.

Monday, February 25th, at 8.15 p.m.

Lecture, **Polonium,** by Professor W. Fernelius. Joint Meeting with Oxford University Alembic Club and the Royal Institute of Chemistry, to be held in the Physical Chemistry Laboratory.

ST. ANDREWS AND DUNDEE.

Tuesday, February 5th, 1957, at 5 p.m.

Lecture, **Some Recent Developments in the Chemistry of Metallic Surfaces,** by Professor K. W. Sykes, M.A., D.Phil. To be given in the Chemistry Department, Queen's College, Dundee.

Friday, February 8th, at 5.15 p.m.

Lecture, **Liquid-phase Oxidation of Hydrocarbons,** by Dr. G. Twigg. Joint Meeting with the University Chemical Society to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Friday, February 15th, at 5.15 p.m.

Lecture, **Reduction by Metal–Ammonia Systems,** by Professor A. J. Birch, D.Sc., D.Phil. Joint Meeting with Royal Institute of Chemistry and the University Chemical Society, to be held in the Chemistry Department, St. Salvator's College, St. Andrews.

Monday, February 18th, at 5 p.m.

Lecture, **The Photochemical Primary Process,** by Professor W. A. Noyes. To be given in the Chemistry Department, Queen's College, Dundee.

SHEFFIELD.

Thursday, February 14th, 1957, at 7.30 p.m.

Lecture, **Adsorption Hysteresis,** by Professor D. H. Everett, M.B.E., M.A., D.Phil. Joint Meeting with the University Chemical Society and the Royal Institute of Chemistry to be held in the Chemistry Lecture Theatre, The University.

Thursday, February 28th, at 7.30 p.m.

Lecture, **Reduction by Metal–Ammonia Solutions,** by Professor A. J. Birch, D.Sc., D.Phil. Joint Meeting with the University Chemical Society and the Royal Institute of Chemistry, to be held in the Chemistry Lecture Theatre, The University.

SOUTHAMPTON.

Friday, February 1st, 1957, at 5 p.m.

Lecture, **Nuclear Magnetic Resonance Techniques,** by Dr. R. Richards, M.A. Joint Meeting with the University Chemical Society and the Royal Institute of Chemistry, to be held in the Chemistry Department, The University.

SOUTH WALES.

Monday, February 18th, 1957, at 5.30 p.m.

Lecture, **Recent Advances in Acetylene Chemistry,** by Professor R. A. Raphael, D.Sc., F.R.I.C. To be given in the Chemistry Department, University College, Cardiff.

Tuesday, February 19th, at 6 p.m.

Lecture, **Recent Advances in Acetylene Chemistry,** by Professor R. A. Raphael, D.Sc., F.R.I.C. Joint Meeting with the University College of Swansea Chemical Society to be held in the Chemistry Department, University College, Swansea.

OFFICIAL ANNOUNCEMENTS

DEATHS.

The Council regrets to announce the deaths of the following Fellows:

	Elected.	Died.
William Herbert Barraclough (Bristol, 7)	Feb. 16th, 1888.	Sept. 20th, 1956.
William Charles Dewey (London, S.W.1)	July 24th, 1950.	Oct. 10th, 1956.
David Paton Grubb (Barnsley)	Dec. 6th, 1906.	June 30th, 1956.
Siddons Siddons Wilson (Bristol)	Feb. 20th, 1913.	July 1st, 1956.

CONGRATULATIONS.

The President has conveyed the congratulations of the Society to Sir Cyril Hinshelwood (Past-President) and to Professor Nikolai Semenov (Honorary Fellow) on the joint award of the Nobel Prize for Chemistry for 1956.

Congratulations have also been conveyed to the following Fellows on the award of Medals announced by the Royal Society:

Royal Medal.

Dr. Dorothy M. Hodgkin.

Davy Medal.

Professor R. D. Haworth.

Rumford Medal.

Dr. F. P. Bowden.

ACKNOWLEDGMENTS.

Acknowledgment is made of a gift of the Society's publications from Dr. A. E. Stubbs.

ELECTION OF NEW FELLOWS.

The following 22 candidates were elected Fellows of the Society on November 15th, 1956:

Anthony Derek John Balon.
Enrique Batres.
Eric Beanland.
Charles Edward Berkoff.
Barry Tebbutt Brown.
Hugh Douglas Cossey.
David Brian Cowell.
Joseph Brun Di Giorgio.
John Michael Groocock.
Raymond John Grout.
Charles Dennis Hall.
Joseph Thomas Maddern.
Kenneth Wintle Morcom.
Taro Nishiwaki.
Arthur Graham Robinson.
Dietmar Seyferth.
Audrey Taylor Smith.
Douglas Swift.
James Welch Taylor.
David William Theobald.
Chelakara Sivarama Vaidyanathan.
Peter Frederick Wagner.

VACANCIES ON COUNCIL.

In accordance with the Bye-laws, the following vacant places on the Council fall due to be filled at the Annual General Meeting to be held in Cambridge on Thursday, 11th April, 1957.

Office.	*No. of Vacancies.*	*Names of Members who are to retire.*
Honorary Secretary	ONE	Dr. L. E. Sutton
Vice-Presidents who have not filled the Office of President	THREE	Professor E. R. H. Jones Dr. R. P. Linstead Professor H. W. Melville
Elected Ordinary Members of Council:		
Constituency I (South-East England)	TWO	Dr. H. M. N. H. Irving Dr. W. Gerrard
Constituency II (Central and South-West England and South Wales)	ONE	Professor H. D. Springall
Constituency III (North-West England, North Wales, and Isle of Man)	ONE	Professor H. N. Rydon
Constituency IV (North-East England)	ONE	Dr. C. C. Addison
Constituency V (Scotland)	ONE	Professor J. M. Robertson
Constituency VI (Ireland)	ONE	Dr. V. C. Barry

With the exception of Dr. W. Gerrard, who was appointed under Bye-law 42, the members who are to retire are not eligible for re-election to the same Office until a lapse of one year.

No vacancy arises for the Office of President.

In accordance with Bye-law 24, the Council has nominated Professor M. J. S. Dewar to fill the vacancy in the Office of Honorary Secretary. Nominations by Fellows for the Offices of Honorary Secretary and of Vice-Presidents who have not filled the Office of President should be made in writing and must be *signed by at least twenty Fellows*.

Fellows resident in a constituency may nominate any Fellow resident in that constituency for election to the Council to fill a vacancy among Elected Ordinary Members of Council allotted to that constituency. Every such nomination must be in writing *signed by at least fifteen Fellows resident in that constituency*.

Fellows may obtain forms of nominations from the General Secretary and should state the vacancy for which they are requested. Every nomination must relate to one vacant place only, and must be accompanied by a signed declaration by the nominee that he is willing to accept office, if elected. Nominations must be received by the Society not later than Thursday, February 14th, 1957.

MINUTES OF SCIENTIFIC MEETINGS

Minutes of a

SCIENTIFIC MEETING

held in the Chemistry Department, University College, Gower Street, W.C.1, on Thursday, November 1st, 1956, at 2.30 p.m.

The President, Professor E. L. Hirst, M.A., D.Sc., F.R.S., was in the Chair.

MINUTES.

The minutes of the Scientific Meetings held at Burlington House and at the College of Technology, Manchester, on October 18th and 19th, respectively, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: Agnes McM. Anderson, Elizabeth J. Williamson, Beryl Rickard, A. C. Jain, M. J. Clancy, Joseph Tinsley, Peter F. Lloyd, James R. Turvey, G. L. Mattok, H. Weigel, R. Nery, B. D. Shepherd, Greville Machell, Desmond O'Meara, D. M. W. Anderson, C. A. Lewis, P. G. Ward, George C. Israel.

SYMPOSIUM.

The President called upon Dr. G. R. Barker to take the Chair for the afternoon session of the Symposium entitled "Newer Interpretations of Reactions and Structure in Carbohydrate Chemistry."

The following contributions were made and discussed:

1. "Some Physical Methods used in the Determination of Carbohydrate Structures," by E. J. Bourne (Royal Holloway College, London).
2. "Tosyl Esters and Three-membered Oxide Rings," by J.C. P. Schwarz (University of Edinburgh).
3. "Conformational Aspects of the Formation and Reactions of Certain Cyclic Derivatives of Carbohydrates," by A. B. Foster (University of Birmingham).

The meeting then adjourned.

In the evening the Chair was taken by Professor M. Stacey, Ph.D., D.Sc., F.R.S.

The following papers were read and discussed:

1. "Hydrolysis of Glycosides," by W. G. Overend (Birkbeck College, London).
2. "Reactions of Halogeno-sugars," by R. U. Lemieux (University of Ottawa).

At the close of the discussion, the Chairman expressed the thanks of the Society to the contributors to the Symposium and to the University College authorities for the use of the Lecture Theatre.

Minutes of a

SCIENTIFIC MEETING

held at Burlington House, on Thursday, November 15th, 1956, at 7.30 p.m.

The President, PROFESSOR E. L. HIRST, M.A., D.Sc., F.R.S., was in the Chair.

MINUTES.

The Minutes of the Scientific Meeting held at the University College, London, W.C.1, on Thursday, November 1st, 1956, were read, and were confirmed and signed.

FORMAL ADMISSION OF FELLOWS.

The following were admitted Fellows of the Society: L. C. Leitch, J. Cymerman-Craig.

SCIENTIFIC COMMUNICATIONS.

The President expressed his pleasure in presiding at a meeting of the Society to commemorate the 70th Birthday of Sir Ian Heilbron, D.S.O., D.Sc., LL.D., F.R.S., Past-President.

The following papers were presented:

"The Aporphine Series. Part II. Application of the Bischler–Napieralski Reaction to *o*-Nitrophenyl-*N*-phenethylacetamides." By D. H. Hey and A. L. Palluel.

"Chemistry of the Higher Fungi. Part VI. Isomerisation Reactions of Naturally-occurring Allenes." By J. D. Bu'Lock, E. R. H. Jones, P. R. Leeming, and J. M. Thompson.

"The Structure of Pulcherrimin" and "Pulcherrimin—a Synthesis of 1 : 4-Dihydroxy-2 : 5-dioxopiperazines." By A. H. Cook and C. A. Slater.

At the conclusion Sir Ian Heilbron expressed his warm appreciation of the Society's action in holding this meeting.

LIST OF APPLICATIONS FOR FELLOWSHIP

(Fellows wishing to lodge objection to the election of these candidates should communicate with the Honorary Secretaries within ten days of the date of publication of the Journal *for December, 1956. Such objections will be treated as confidential. The forms of application are available in the Library.)*

Allen, William. British. Ferens Hall, Harland Way, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, J. J. Kipling.

Arnold, Derrick Freeborough. British. Ferens Hall, Harland Way, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, N. B. Chapman.

Badger, Alan George. British. Room 45A, Ferens Hall, Harland Way, Cottingham, E. Yorks. Student at Hull University. *Signed:* G. W. Gray, N. B. Chapman.

Bateman, Alan William Thomas. British. 58A The Woodlands, London, S.E.13. Technical Assistant. *Signed by:* P. V. Smith, jun., R. W. Morton.

Bell, David William. British. 85A, Victoria Road, Leeds, 6. Student. *Signed by:* C. J. Willis, H. C. Clark.

Bowden, Keith. British. Ferens Hall, Harland Way, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, J. J. Kipling.

Britton, David John. British. C1, Old Court, Clare College, Cambridge. Student. *Signed by:* R. N. Haszeldine, C. B. Reese.

Brookes, John Henry. British. 19, Queen Street, Pant, Dowlais, Glam. Student. *Signed by:* E. E. Ayling, G. H. R. Summers.

Cairncross, Ian Macleod. British. 142, St. Stephen Street, Edinburgh. Student. *Signed by:* G. O. Aspinall, A. McM. Anderson.

Cairns, John Francis. British. 27, Woodville Gardens, Ilford, Essex. Student. *Signed by:* K. W. Sykes, M. F. Ansell.

Catlow, David Brian. British. 3, Winchester Road, Ilford, Essex. Student at Queen Mary College. *Signed by:* K. W. Sykes, W. J. Hickinbottom.

Chalmers, Robert Alexander, B.Sc. (Manc.), Ph.D. (Edin.). British. 9, Balgownie Road, Bridge of Don, Aberdeenshire. University Lecturer. *Signed by:* R. Belcher, J. E. Fildes.

Chetwyn, Alan, B.Sc. (Wales), A.R.I.C. British. 44, Kimberley Road, Pen-y-Lan, Cardiff, Glam. Research Student. *Signed by:* J. W. Bayles, A. R. Pinder.

Cliffe, Eric Edward, B.A. (Cantab.). British. Nuffield Laboratory of Ophthalmology, Walton Street, Oxford. Research Student. *Signed by:* S. G. Waley, F. M. Brewer.

Cornford, Pauline Valerie. British. Thwaite Hall, Thwaite Street, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, J. J. Kipling.

Coombs, Robert Victor. British. 6, Cheapside, Brighton, Sussex. Student at Queen Mary College. *Signed by:* K. W. Sykes, W. J. Hickinbottom.

Cowen, Raymond Arthur, B.Sc. (Liv.). British. 22, Hawthorne Grove, Great Carleton, Poulton-le-Fylde, Blackpool, Lancs. Research Student. *Signed by:* C. C. Barker, G. W. Gray.

Deb, Satyendra Kumar, M.Sc. (Dacca). Pakistani. Gonville and Caius College, Cambridge. Research Student. *Signed by:* A. D. Yoffe, F. P. Bowden.

Eastaugh, Derek John. British. 38, Church Street, Hatfield, Herts. Student. *Signed by:* T. J. Barnes, T. E. Rogers.

Frost, John Stuart. British. 25, Woodside View, Greetland, Nr. Halifax. Yorks. Student at Queen's College, Oxford. *Signed by:* R. E. Richards, J. W. Linnett.

Gibson, Michael David. Student. British. 8, Hartham Road, Isleworth, Middlesex. Student at Queen Mary College. *Signed by:* W. J. Hickinbottom, K. W. Sykes.

Gray, Frank Alexander. Australian. 9, Donnelly Road, Naremburn, New South Wales, Australia. Research Student. *Signed by:* I. G. Ross, T. Iredale.

Hallas, Geoffrey, B.Sc. (Hull). British. 53, Tom Lane, Crosland Moor, Huddersfield, Yorks. Research Student. *Signed by:* G. W. Gray, K. Clarke.

Hatch, Frank. British. Hillmount, Hiraddug Road, Dyserth, Rhyl, Flintshire. Student. *Signed by:* E. E. Ayling, G. H. R. Summers.

Hobday, Elizabeth Ann. British. 17, Fitzroy Road, Swindon, Wilts. Student. *Signed by:* R. E. Richards, H. Irving.

Hunt, John Anthony, B.A. (Cantab.). British. 26, Tenison Avenue, Cambridge. Research Assistant at Medical Research Council Unit, Cambridge. *Signed by:* V. M. Ingram, J. E. Downes.

Ibbotson, Arthur, B.Sc. (Lond.). British. 29, Pendrill Street, Beverley Road, Hull, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, K. Clarke.

Irvine, Dennis Horace, B.Sc. (Leeds), Ph.D. (Cantab.). British. Department of Chemistry, University College, Ibadan, Nigeria. Lecturer. *Signed by:* C. W. L. Bevan, J. Hirst.

Jackson, Richard Anthony, B.A. (Oxon.). British. 18, Linden Drive, Evington, Leicester. Research Student at Balliol College. *Signed by:* R. E. Richards, R. P. Bell.

Jamoos, Jalal Jamil Mansoor. Iraqi. 23, Sketty Road, Uplands, Swansea. Student. *Signed by:* D. A. Long, R. H. Davies.

Jones, Richard Alan. British. 6, Westfield Road, Bedford, Beds. Student. *Signed by:* R. E. Richards, A. R. Katritzky.

Keen, Ian Montgomery. British. Kiln Farm, Marden, Tonbridge, Kent. Student at Queen Mary College. *Signed by:* K. W. Sykes, T. R. Layzell.

Lawlor, John Michael. British. Flat 11, Tooting Police Station, Mitcham Road, London, S.W.17. Undergraduate at the Royal College of Science. *Signed by:* J. A. Elvidge, P. F. Todd.

Lemon, David. British. 136, Princes Avenue, London, W.3. Flavour Chemist. *Signed by:* W. H. Shilling, E. S. Maurer.

Lewis, David, B.Sc. (Hull). British. 111, Fairfax Avenue, Hull, E. Yorks. Research Student. *Signed by:* C. C. Barker, G. W. Gray.

Lown, James William, B.Sc. (Lond.), A.R.C.S. British. 3, The Links, Seaton Sluice, Whitley Bay, Northumberland. Post-graduate Student at Imperial College. *Signed by:* L. M. Jackman J. A. Elvidge.

McEvan, Thomas. British. 2, Thornacre Crescent, Wrose, Shipley, Yorks. Chemical Manufacturer. *Signed by:* N. Logan, E. Markham.

McWhinnie, William Robin. British. 32, Sutherland Avenue, Welling, Kent. Student. *Signed by:* K. W. Sykes, E. A. Lucken.

McWilliam, Ian Robert. British. Tormore, Thornhill Avenue, Elderslie, Renfrewshire. Student. *Signed by:* C. T. Ironside, R. H. B. Galt.

Mason, Frank John. British. Ferens Hall, Harland Way, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, J. J. Kipling.

Mather, Joseph Glendinning, B.Sc. (Lond.). British. 19, Pearson Avenue, Hull, E. Yorks. Research Student. *Signed by:* J. Shorter, G. W. Gray.

Mitchell, David Lawrence, B.Sc. (Kingston, Canada). Canadian. Department of Chemistry, Gordon Hall, Queen's University, Kingston, Ontario, Canada. Graduate Student. *Signed by:* N. K. Matheson, T. J. Painter.

Moffatt, John Gilbert, B.A., M.Sc., and Ph.D. (British Columbia). Canadian. British Columbia Research Council, University of British Columbia, Vancouver 8, British Columbia, Canada. Research Chemist. *Signed by:* H. G. Khorana, G. M. Tener.

Morantz, Daniel Joseph, M.Sc. (McGill), Ph.D. (Manc.). Canadian. 227, Barnsley Road, Sheffield, 4. Honorary Lecturer at Sheffield University. *Signed by:* G. Porter, H. J. V. Tyrrell.

Muhammad, Sultan, M.Sc. (Panjab). Pakistani. Organic Chemistry Department, The University, Manchester, 13. Student. *Signed by:* G. D. Meakins, R. N. Speake.

Newham, John, B.Sc. (Hull). British. 92, Edgecumbe Street, Newland Avenue, Hull. Research Student. *Signed by:* G. C. Bond, G. W. Gray.

Peapell, Margaret. British. Thwaite Hall, Thwaite Street, Cottingham, E. Yorks. Student at Hull University. *Signed by:* G. W. Gray, J. J. Kipling.

Perry, Reginald Gilbert. British. 249, Southcroft Road, Streatham, London, S.W.16. Student at Imperial College. *Signed by:* J. A. Elvidge, R. M. Barrer.

Posner, Ruth, B.Sc. (Lond.). British. 21, Norman Avenue, Tunstall, Stoke on Trent. Research Student at Queen Mary College. *Signed by:* M. J. S. Dewar, C. M. French.

Rae, Anthony Charles, B.Sc.Tech. (Manc.). British. 5, Cliff Grove, Heaton Moor, Stockport, Cheshire. Research Student at Manchester University. *Signed by:* H. N. Rydon, T. K. Walker.

Roderick, Howell Rhys. British. Gwydderig, North Road, Whitland, Carmarthenshire. Student. *Signed by:* E. E. Ayling, G. H. R. Summers.

Rogers, Henry Joseph, B.Sc. (Sheffield). 71, Huntingtower Road, Ecclesall, Sheffield, 11. Student. *Signed by:* R. D. Haworth, D. T. Elmore.

Schimelpfenig, Clarence William, jun., M.S. (North Texas State Coll.). American. 211, Noyes Laboratory, University of Illinois, Urbana, Illinois, U.S.A. Graduate Student. *Signed by:* D. Y. Curtin, N. J. Leonard.

Shimoyama, Kichiro, M.Chem. (Tokyo). Japanese. c/o Meguro Laboratory, Mitsui Chemical Industry Co. Ltd., 1–839, Nakameguro, Meguro-ku, Tokyo, Japan. Manager of Meguro Laboratory. *Signed by:* T. Ohta, H. Okeda.

Sperry, John Arthur. British. Station House, Asfordby Hill, Melton Mowbray, Leics. Student at Imperial College. *Signed by:* J. A. Elvidge, R. M. Barrer.

Stamp, Anthony, B.Sc. (Hull). British. 25, Ventnor Street, Hull, Yorks. Student. *Signed by:* C. C. Barker, G. W. Gray.

Stewart, Michael Simon. British. 27, Ashcombe Gardens, Edgware, Middlesex. Student. *Signed by:* N. Lewin, J. Hudec.

Taft, Robert W., jun., M.S. (Kansas), Ph.D. (Ohio). American. Department of Chemistry, Pennsylvania State University, University Park, Penna., U.S.A. Professor of Chemistry. *Signed by:* A. P. Wolf, D. R. Christman.

Troman, John Neville. British. 14, Moorland Avenue, Lincoln. Student at Nottingham University. *Signed by:* T. J. King, D. Shooter.

Utley, James Henry Paul. British. 119, Castle Hill, Reading, Berks. Student at Hull University. *Signed by:* G. W. Gray, K. Clarke.

Walmsley, Robert Seddon, B.A. (Oxon.). British. Ingledene, Junction Road, Deane, Bolton, Lancs. Research Student at Oxford University. *Signed by:* R. E. Richards, J. H. Barltrop.

Walters, Stephen Terrey. British. Hotel Bon Port, St. Martin, Guernsey, Channel Islands. Student at Oxford University. *Signed by:* R. E. Richards, L. A. K. Staveley.

Waterfield, William Richard. British. Broughton Villa, Broughton, Nr. Kettering, Northants. Undergraduate at Imperial College. *Signed by:* J. A. Elvidge, L. M. Jackman.

Waterman, Hanneke, B.Sc. (Sydney). British. c/o School of Applied Chemistry, New South Wales University of Technology, Ultimo, New South Wales, Australia. Research Student. *Signed by:* R. L. Martin, I. K. Gregor.

Watson, Peter Frederick, B.Sc. (Nott.). British. Leamington College for Boys, Binswood Avenue, Leamington Spa. School Teacher. *Signed by:* T. J. King, G. Read.

Whiteman, John Leonard, B.Sc. (Lond.). British. 24, The Drive, Tonbridge, Kent. Research Chemist. *Signed by:* D. A. Ginger, J. Wilby.

Wilson, Thomas Michael Binns, B.Sc. (Manc.). British. 10, Farndale Crescent, Middlesbrough. Research Student at Manchester University. *Signed by:* G. D. Meakins, R. N. Speake.

Wood, Alexander. Student. British. 3, Milton Street, Carluke, Lanarkshire. Student at Glasgow University. *Signed by:* C. T. Lewin, J. A. Mair.

Worrall, Brian Michael, B.Sc. (Hull). British. 101, Woodville Road, Boston, Lincs. Research Student. *Signed by:* C. C. Barker, G. W. Gray.

UNDER SPECIAL PROVISION APPERTAINING TO FELLOWS RESIDENT ABROAD.

Shipley, Warwick Grenville Michael, B.Sc. (Sheffield). British. Schafweide, 73, (17a) Mannheim, Germany. Research Chemist. *Signed by:* H. J. V. Tyrrell.

PAPERS ACCEPTED

(List of Papers accepted between October 19th and November 15th, 1956, for publication in the *Journal*.)

" Electrophilic substitution. Part IX. The anomalous nitrations of quinoline." By M. J. S. Dewar and P. M. Maitlis.

" Stability of the glycosidic linkages in carbohydrates." By Winifred G. Wright.

" The preparation of fused triazole systems." By J. D. Bower and F. P. Doyle.

" The photodecomposition of carbon dioxide and of ammonia by xenon 1470 Å radiation." By H. Jucker and (Sir) Eric K. Rideal.

" The oxidation of monoethenoid fatty acids and esters. Catalytic oxidation of ketol derivatives of oleic acid." By T. L. Parkinson and J. H. Skellon.

" Spectrophotometric determination of the dissociation constant of hydrogen peroxide." By S. S. Muhammed and T. Navaneeth Rao.

" The products of the interaction of hydrogen selenide and ketones." By D. S. Margolis and R. W. Pittman.

The action of bromine–sulphuric acid mixtures on methyl α-D-glucopyranoside." By A. B. Foster and S. V. Vardheim.

" The antisymmetric stretching band of carbodi-imides." By G. D. Meakins and R. J. Moss.

" The chemistry of nitrosyl complexes. Part III. Evidence for compound formation in liquid nitrosyl chloride from tracer studies." By J. Lewis and D. B. Sowerby.

" Infrared spectra and polar effects. Part V. Carbonyl–carbonyl interactions." By L. J. Bellamy and R. L. Williams.

" Infrared spectra and polar effects. Part VI. Internal and external spectral relationships." By L. J. Bellamy and R. L. Williams.

" The reaction of anthracene with benzyl radicals." By A. L. J. Beckwith and William A. Waters.

" Quantitative aspects of the base-catalysed halogenation of aliphatic ketones. Part II. Iodination of non-methyl ketones." By C. F. Cullis and M. H. Hashmi.

" Chalcones and related compounds. Part I. Preparation of nitro-, amino-, and halogeno-chalcones." By W. Davey and J. R. Gwilt.

" Chalcones and related compounds. Part II. Addition of thiols and esters to the chalcone system." By W. Davey and J. R. Gwilt.

" Chalcones and related compounds. Part III. Addition of benzene analogues to the chalcone system." By W. Davey and J. R. Gwilt.

" Alkyl migration in some organophosphorus amidates." By J. I. G. Cadogan.

" 2-Mercaptoglyoxalines. Part XI. The preparation of mixed 1 : 5-disubstituted 2-mercaptoglyoxalines and the corresponding thiazolo(3′ : 2′-1 : 2)glyoxalines." By Alexander Lawson and H. V. Morley.

" Toxic constituents of the Australian finger cherry, *Rhodomyrtus macrocarpa* Benth." By S. Trippett.

" The detection, by means of anthracene, of free radicals formed in " abnormal " reactions of Grignard reagents." By R. O. C. Norman and W. A. Waters.

" Addition of methyl radicals to substituted benzenes." By W. J. Heilman, A. Rembaum, and M. Szwarc.

" Organosilicon compounds. Part XIX. Medium effects in the reaction between trimethylsilylmethylbenzoate ions and hydroxide ion." By C. Eaborn and S. H. Parker.

" Structure of compounds of ferrocyanide type. Part II. Crystal structure of β-tetramethyl ferrocyanide." By R. Hulme and H. M. Powell.

" A search for new trypanocides. Part IV. Some derivatives of 4-amino-6-amino-methylquinaldine and 1 : 2-di-(4-aminoquinald-6-yl)ethylene." By J. N. Ashley and M. Davis.

" The dipole moment of the helium hydride molecule-ion, HeH^{2+}." By B. F. Gray and H. O. Pritchard.

" The nature and stability of the complex ions formed by ter-, quadri-, and sexa-valent

plutonium ions with ethylenediaminetetra-acetic acid. Part I. pH Titrations and ion-exchange studies." By J. K. FOREMAN and T. D. SMITH.

" The nature and stability of the complex ions formed by ter-, quadri-, and sexa-valent plutonium ions with ethylenediaminetetra-acetic acid. Part II. Spectrophotometric studies." By J. K. FOREMAN and T. D. SMITH.

" The paper chromatography of cyclitols." By S. J. ANGYAL, D. J. MCHUGH, and P. T. GILHAM.

" Absorption spectra of some sulphoxides in the near ultraviolet region." By G. LEANDRI, A. MANGINI, and R. PASSERINI.

" Electron donor and acceptor complexes with aromatic systems. Part V. Polarisation bonding in solid complexes formed by some heterocyclic aromatic molecules." By W. SLOUGH and A. R. UBBELOHDE.

" Studies in pyrolysis. Part VIII. Competitive routes in the pyrolysis of esters : alkylene and alkylidene dibenzoates and some related substances." By R. J. P. ALLAN, E. JONES, and P. D. RITCHIE.

" A conductimetric study of acid–base interactions in non-aqueous media." By P. J. R. BRYANT and A. W. H. WARDROP.

" Colour and constitution. Part I. The effect of methyl substitution on the ultraviolet spectra of alternant hydrocarbons." By DAVID PETERS.

" Syntheses from phthalimido-acids. Part VII. Oxazolones and other intermediates in the synthesis of phthalylpeptides, and an investigation of maleic acid derivatives of amino-acids." By F. E. KING, J. W. CLARK-LEWIS, ROY WADE, and (in part) W. A. SWINDIN.

" Syntheses from phthalimido-acids. Part VIII. Synthesis of glutathione by a new route to cysteinyl-peptides." By F. E. KING, J. W. CLARK-LEWIS, and ROY WADE.

" Syntheses from phthalimido-acids. Part IX. Model compounds for a synthesis of glutathione, and phthalyl-L-glutamic anhydride as a source of α-glutamyl-peptides." By F. E. KING, J. W. CLARK-LEWIS, and ROY WADE.

" A total synthesis of (±)-ferruginol." By F. E. KING, T. J. KING, and J. G. TOPLISS.

" The preparation of 2 : 2-dimethyl- and 2 : 2 : 6-trimethyl*cyclo*hexanone." By F. E. KING, T. J. KING, and J. G. TOPLISS.

" Triterpenes and related compounds. Part XXX. The relative stabilities of ring-A unsaturated hydrocarbons derived from 3 : 4-dimethylcholestane and 3-methyl-24-norurs-12-ene." By J. L. BETON, T. G. HALSALL, E. R. H. JONES, and P. C. PHILLIPS.

" The preparation of 2-(5-methyl-1-naphthyl)ethyl bromide." By J. C. BARDHAN, D. NASIPURI, and D. N. MUKHERJI.

" Nucleophilic displacement reactions in aromatic systems. Part VI. Influence of nuclear alkyl groups in the aromatic system. Kinetics of the reactions of chlorodinitrotoluenes and related compounds with piperidine, aniline, and ethoxide ions in ethanol, and with methoxide ions in methanol." By B. CAPON and N. B. CHAPMAN.

" Polymerisation of thiophen derivatives. Part V. Some condensations of nitrothionaphthen 1 : 1-dioxides." By W. DAVIES and Q. N. PORTER.

" Vegetable oils. Part VI. The component acids of ergot oil." By K. E. BHARUCHA and F. D. GUNSTONE.

" Fatty acids. Part V. Applications of the Woodward *cis*-hydroxylation procedure to long-chain olefinic compounds. By F. D. GUNSTONE and L. J. MORRIS.

" Nyctanthic acid, a constituent of *Nyctanthes arbor-tristis*, Linn." By J. H. TURNBULL, SHYAM KISHORE VASISTHA, W. WILSON, and R. WOODGER.

" Actinomycin. Part III. The reaction of actinomycin with alkali." By S. J. ANGYAL, E. BULLOCK, W. G. HANGER, W. C. HOWELL, and A. W. JOHNSON.

" Actinomycin. Part IV. An oxidative degradation of actinomycin B." By E. BULLOCK and A. W. JOHNSON.

" Photochemical transformations. Part I. Some preliminary investigations." By D. H. R. BARTON, P. DE MAYO, and MOHAMMED SHAFIQ.

" Niobium and tantalum pentachlorides and their binary system." By J. B. AINSCOUGH, R. J. W. HOLT, and F. W. TROWSE.

" The preparation of cyclic ketones by use of trifluoroacetic anhydride." By R. J. FERRIER (in part) and J. M. TEDDER.

" Complexes involving tervalent iron and orthophosphoric acid. Part IV. Evidence for the formation of polynuclear complexes from ion-exchange experiments." By A. HOLROYD and J. E. SALMON.

" Constitution of dalbergin. Part II." By V. K. AHLUWALIA and T. R. SESHADRI.

" Polyfluoroalkyl compounds of silicon. Part II. Free-radical reaction of dialkylsilanes with fluoro-olefins." By A. M. GEYER and R. N. HASZELDINE.

" Curvularin. Part II. The constitution of an aromatic degradation product and the partial structure of curvularin." By O. C. MUSGRAVE.

" The relation between configuration and conjugation in diphenyl derivatives. Part VIII. Some compounds derived from 2 : 2′-diacetyldiphenyl." By G. H. BEAVEN and E. A. JOHNSON.

" Infrared absorption bands associated with the NH group. Part I. Some secondary aromatic amines." By D. HADŽI and (MISS) M. ŠKRBLJAK.

" Infrared absorption bands associated with the NH group. Part II. Some secondary thioamides and *N*-methyltoluenesulphonamide." By D. HADŽI.

" Infrared spectra of natural products. Part VII. The identification and location of ethylenic double bonds in pentacyclic triterpenoids." By A. R. H. COLE and D. W. THORNTON.

" Red-seaweed polysaccharides. Part II. *Porphyra capensis* and the separation of D- and L-galactose by crystallisation." By J. R. NUNN and (MRS.) M. M. VON HOLDT.

" Structure of gentianine." By T. R. GOVINDACHARI, K. NAGARAJAN, and S. RAJAPPA.

" Long-range effects in alicyclic systems. Part II. The rates of condensation of some triterpenoid ketones with benzaldehyde." By D. H. R. BARTON, A. J. HEAD, and P. J. MAY.

" Exchange studies of certain chelate compounds of the transitional metals. Part II. The rate of racemisation and dissociation of the tris-(1 : 10-phenanthroline)nickel(II) ion." By R. G. WILKINS and M. J. G. WILLIAMS.

" Tracer studies in ester hydrolysis. Part IV. The hydrolyses of diphenylmethyl formate and acetate." By C. A. BUNTON, J. N. E. DAY, R. H. FLOWERS, P. SHEEL, and J. L. WOOD.

" Conversion of methyltrichlorosilane into chloromethyl derivatives of silane." By H. D. KAESZ and F. G. A. STONE.

" Preparation of glycol monoesters of fatty acids with the use of boron intermediates." By L. HARTMAN.

" Bromination of triterpenoids of the oleanane and ursane series." By O. P. ARYA and R. C. COOKSON.

" 1 : 2-5 : 6-Di-*O*-*iso*propylidene-α-D-glucofuranose 3-(methyl sulphate)." By A. B. FOSTER and E. B. HANCOCK.

" The kinetics and mechanisms of aromatic halogen substitution. Part IV. Rates of bromination of benzene and of hexadeuterobenzene by aqueous hypobromous acid containing perchloric acid." By P. B. D. DE LA MARE, T. M. DUNN, and J. T. HARVEY.

" Chlorophyll and related compounds. Part VI. The synthesis of octaethylchlorin." By ULLI EISNER, ALEKSANDRA LICHTAROWICZ, and R. P. LINSTEAD.

" Polonium monosulphide." By K. W. BAGNALL and D. S. ROBERTSON.

" 6β-Hydroxy-3 : 5-*cyclo*pregnan-20-one and some related compounds." By D. K. PATEL, V. PETROW, and (MRS.) I. A. STUART-WEBB.

" New complexes containing tellurium." By E. E. AYNSLEY and W. A. CAMPBELL.

" Mandelamidines as potential bronchodilators." By N. W. BRISTOW.

" α-Methyltropic acid—a correction." By R. FOSTER and H. R. ING.

" The cholestane-2 : 3-diols." By H. B. HENBEST and M. SMITH.

" Some steroidal 1 : 4-diene-3 : 11-diones and 1 : 4 : 6-triene-3 : 11-diones." By D. N. KIRK, D. K. PATEL, and V. PETROW.

" Configurational studies in synthetic analgesics : the synthesis of (−)-methadone from D-(−)-alanine." By A. H. BECKETT and N. J. HARPER.

"Experiments on the synthesis of the pyrethrins. Part XII. *cyclo*Hexenone analogues of cinerone and pyrethrone." By A. J. B. EDGAR, S. H. HARPER, and M. A. KAZI.

"The hemicelluloses of loblolly pine (*Pinus taèda*) wood. Part I. The isolation of five oligosaccharide fragments." By J. K. N. JONES and T. J. PAINTER.

"Infrared absorption of 1 : 2-disubstituted *cis*-ethylenic centres." By H. B. HENBEST, G. D. MEAKINS, B. NICHOLLS, and R. A. L. WILSON.

"Detection of the epoxide group by infrared spectroscopy." By H. B. HENBEST, G. D. MEAKINS, B. NICHOLLS, and K. J. TAYLOR.

"The stereochemistry of the tropane alkaloids. Part X. The total synthesis of valeroidine." By IRÉN VINCZE, JÓZSEF TÓTH, and GÁBOR FODOR.

"The stereochemistry of the 3 : 5-*cyclo*cholestan-6-yl amines." By D. E. EVANS and G. H. R. SUMMERS.

"*iso*Cyanates. Part III. Benzoyl *iso*cyanate." By C. L. ARCUS and B. S. PRYDAL.

ADDITIONS TO THE LIBRARY

Tal vid Herr Carl Wilhelm Scheeles, by C. J. Ahlstrom. (Inserted—Programme of ceremony commemorating the 150th anniversary of Scheeles' death, held at Koping, 1936.) Svenska Tryckeriaktiebolaget. 1936. (Presented by Dr. Maddison.)

Medicinal chemistry; a series of reviews prepared under the auspices of the Division of Medicinal Chemistry of the American Chemical Society; edited by F. F. Blicke and R. H. Cox. Vol. III. John Wiley and Sons, Inc., 1956.

Hydrogen ions: their determination and importance in pure and industrial chemistry, by H. T. S. Britton. Vol. 2. 4th Edn. Chapman & Hall. 1956.

Sir William Henry Perkin, by W. Voegelin *et al.* (*CIBA Review*, 1956, (115), June, pp. 2—49) CIBA Ltd. 1956. (Presented by the Publishers.)

Annual review of microbiology, edited by C. E. Clifton, S. Raffel, and R. Y. Stanier. Vol. 10. Annual Reviews, Inc. 1956.

Organometallic compounds, by G. E. Coates. Methuen. 1956.

Actas y trabajos del Cuarto Congreso Peruano de Quimica, Lima, 1953. Universidad Nacional Mayor de San Marcos. 1956. (Presented by the Publishers.)

Advances in chemical engineering, edited by T. B. Drew and J. W. Hoopes. Vol. I. Academic Press, Inc. 1956.

Advances in catalysis and related subjects, edited by W. G. Frankenburg *et al.* Vol. 8. Academic Press Inc. 1956.

Handbuch der analytischen Chemie, edited by W. Fresenius and G. Jander. Vol. 2. Qualitative Nachweisverfahren. Part 8 bA. Elemente der achten Nebengruppe. I. Eisen; Kobalt; Nickel; edited by B. Grüttner and H. Hahn. Springer-Verlag. 1956.

pH measurements: their theory and practice, by V. Gold. Methuen. 1956.

Vitamins and hormones: advances in research and applications, edited by R. S. Harris, G. F. Marrian, and K. V. Thimann. Vol. 14. Academic Press Inc. 1956.

Progress in radiobiology: proceedings of the Fourth International Conference on Radiobiology held in Cambridge, 1955, edited by J. S. Mitchell, B. E. Holmes and C. L. Smith. Oliver and Boyd. 1956.

Special lectures in biochemistry, 1954—1955. University College, London University. 1956. (Presented by the Department of Biochemistry, University College.)

Joseph Priestley and the Birmingham riots, by R. E. W. Maddison and F. R. Maddison. (Reprinted from *Notes and Records of the Royal Society of Londo-*, 1956, **12**, No. 1.) Royal Society. 1956. (Presented by Dr. Maddison.)

Supplement to Mellor's comprehensive treatise on inorganic and theoretical chemistry, by J. W. Mellor. Suppl. II, part I. Longmans, Green and Co. 1956. (Presented by the Publishers.)

The determination of niobium and molybdenum in uranium terniary alloys, by G. W. C. Milner, G. A. Barnett, and A. Bacon. (Atomic Energy Research Establishment C/R 1805.) Atomic Energy Research Establishment. 1956.

Recent progress in hormone research: proceedings of the Laurentian Hormone Conference 1955, edited by G. Pincus. Vol. 12. Academic Press Inc. 1956.

Electrochemistry: principles and applications, by E. C. Potter. Cleaver-Hume Press, Ltd. 1956. (Presented by the Author.)

Fortschritte der Chemie organischer Naturstoffe, edited by L. Zechmeister. Vol. 13. Springer-Verlag. 1956.

LOCAL REPRESENTATIVES OF THE CHEMICAL SOCIETY

Aberdeen.	R. H. Thomson, Ph.D., F.R.I.C., Chemistry Department, The University, Old Aberdeen.
Australia.	K. H. Pausacker, M.Sc., D.Phil., Chemistry Department, University of Melbourne, Carlton, N. 3, Victoria, Australia.
,,	Professor A. E. Alexander, M.A., Ph.D., Chemistry Department, N.S.W. University of Technology, Sydney, N.S.W., Australia.
Birmingham.	J. C. Tatlow, B.Sc., Ph.D., Department of Chemistry, The University, Edgbaston, Birmingham, 15.
Bristol.	P. Woodward, B.Sc., Ph.D., Chemistry Department, The University, Woodland Road, Bristol.
Cambridge.	R. N. Haszeldine, M.A., D.Sc., F.R.I.C., University Chemical Laboratory, Pembroke Street, Cambridge.
Canada.	Professor J. K. N. Jones, M.Sc., Ph.D., A.R.I.C., Queen's University, Kingston, Ontario.
Cardiff.	A. R. Pinder, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, University College, Cardiff.
Ceylon.	G. P. Wannigama, B.Sc., Ph.D., Department of Chemistry, The University, Colombo, Ceylon.
Edinburgh.	G. O. Aspinall, B.Sc., Ph.D., Chemistry Department, King's Buildings, West Mains Road, Edinburgh.
Exeter.	K. Schofield, B.Sc., Ph.D., F.R.I.C., Department of Chemistry, The University, Exeter.
Glasgow.	D. S. Payne, B.Sc., Ph.D., A.R.I.C. Chemistry Department, The University, Glasgow, W.2.
Hull.	G. W. Gray, B.Sc., Ph.D., Chemistry Department, The University, Hull.
India.	Professor T. R. Seshadri, M.A., Ph.D., F.R.I.C., Department of Chemistry, The University, Delhi, India.
Irish Republic.	D. O Tuama, M.Sc., Ph.D., F.I.C.I., Medical Research Council of Ireland, The Laboratories, Trinity College, Dublin.
Leeds.	E. Rothstein, Ph.D., D.Sc., A.R.C.S., Organic Chemistry Department, The University, Leeds, 2.
Liverpool.	A. K. Holliday, B.Sc., Ph.D., Department of Physical and Inorganic Chemistry, The University, Liverpool.
,,	D. W. Broad, Ph.D., A.R.I.C., Imperial Chemical Industries Limited, General Chemicals Division, Cunard Building, Liverpool, 3.
Manchester.	A. C. Farthing, M.A., B.Sc., Imperial Chemical Industries Limited, Hexagon House, Blackley, Manchester, 9.
,,	G. D. Meakins, M.A., D.Phil., Chemistry Department, The University, Manchester, 13.
Newcastle and Durham.	G. Kohnstam, B.Sc., Ph.D., The University Science Laboratories, South Road, Durham.
	F. J. McQuillin, M.A., D.Phil., Chemical Department, King's College, Newcastle upon Tyne.
New Zealand.	Professor S. N. Slater, M.Sc., D.Phil., A.R.I.C., Chemistry Department, Victoria University College, Wellington, New Zealand.
Northern Ireland.	R. G. R. Bacon, Ph.D., A.R.C.S., Chemistry Department, Queen's University, Belfast.
North Wales.	J. E. McKail, Ph.D., Department of Chemistry, University College of North Wales, Bangor.
Nottingham and Leicester	T. J. King, B.Sc., M.A., D.Phil., Chemistry Department, The University, University Park, Nottingham.
,,	E. R. A. Peeling, B.Sc., Ph.D., University College, Leicester.
Oxford.	R. E. Richards, M.A., D.Phil., Lincoln College, Oxford.
Pakistan.	M. I. D. Chughtai, M.Sc.Tech., Ph.D., A.R.I.C., Punjab University Institute of Chemistry, The Mall, Lahore, Pakistan.
St. Andrews and Dundee.	C. Horrex, M.Sc., Ph.D., Chemistry Department, The University, St. Andrews.
Sheffield.	H. J. V. Tyrrell, M.A., B.Sc., Chemistry Department, The University, Sheffield, 10.
South Africa.	Professor F. L. Warren, Ph.D., F.R.I.C., Department of Chemistry, University of Natal, P.O. Box 375, Pietermaritzburg, South Africa.
Southampton.	Miss Ishbel G. M. Campbell, B.Sc., Ph.D., Department of Chemistry, The University, Southampton.
Swansea.	R. H. Davies, M.Sc., A.R.I.C., Department of Chemistry, University College, Singleton Park, Swansea.